VOL. XXX. NOVEMBER, 1903. NO. 5.

AMERICAN

CHEMICAL JOURNAL

A COMPARATIVE STUDY OF ORTHOSULPHAMINE-BENZOIC ACID AND ORTHOCARBAMINE-BENZENESULPHONIC ACID.[1]

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As methods are available for the preparation of orthosulphaminebenzoic acid, $C_6H_4\begin{cases}COOH\\SO_2NH_2\end{cases}$, and of orthocarbaminebenzenesulphonic acid, $C_6H_4\begin{cases}CONH_2\\SO_2OH\end{cases}$, and neither acid has been studied with especial care, Professor Remsen suggested that I should prepare them in considerable quantity and make a comparative study of them.

Preparation of Orthosulphaminebenzoic Acid.

This acid was first prepared by W. A. Noyes[2] by oxidizing orthotoluenesulphonamide with potassium ferricyanide. He described it as being easily soluble in alcohol and ether and quite readily in cold water. He obtained it in two different

[1] From the author's dissertation submitted, June, 1899, to the Board of University Studies of the Johns Hopkins University, in conformity with the requirements for the degree of Doctor of Philosophy. The investigation was undertaken at the suggestion of Professor Remsen and carried out under his guidance.

[2] This JOURNAL, 8, 176.

forms—fine needles and large prisms, which appeared to belong to the monoclinic system. He states that, when rapidly heated, the acid melts at 165° to 167°, but that, when slowly heated, it melts at 153° to 155°.

The acid can be readily prepared by heating benzoic sulphinide with sodium hydroxide. The sulphinide was purified by the method suggested by Pope,[1] which consists in crystallizing the sulphinide from acetone. The sulphinide is more soluble in hot than in cold acetone. The parasulphaminebenzoic acid, which is sometimes found in benzoic sulphinide as an impurity, is insoluble in acetone. This being the case, it is an easy matter to separate the two substances. The sulphinide used in the following experiments contained scarcely a trace of parasulphaminebenzoic acid, even before it was treated with acetone. One hundred grams of the sulphinide required about 460 grams of acetone.

When the benzoic sulphinide is dissolved in hot acetone, a white, crystalline mass is deposited immediately upon cooling, but if the sulphinide is dissolved in cold acetone and the solution is allowed to evaporate spontaneously, large, colorless rhombohedrons are deposited, some of which are several millimeters in length.

It was found that, when the benzoic sulphinide is treated with sodium hydroxide under the following conditions, the orthosulphaminebenzoic acid is produced in nearly a quantitative yield: Twenty grams of pure benzoic sulphinide are added to a caustic soda solution, prepared by dissolving 15 grams of sodium hydroxide in 500 cc. of water. This solution was evaporated on a water-bath until the sweet taste of the sulphinide could no longer be detected. The solution was allowed to cool and then filtered. The acid was precipitated by means of hydrochloric acid. If the solution is stirred vigorously, after the addition of hydrochloric acid, the acid is precipitated at once in fine crystals. If allowed to stand over night without disturbance, large monoclinic crystals are deposited. After filtering, the acid was dissolved in alcohol,

[1] J. Chem. Soc., 67, 985.

from which it crystallized in large, transparent rhombohedrons.

The acid, when heated slowly, melted at 152°; when heated rapidly, it melted at 159° C (uncorrected). It is quite soluble in alcohol and water. Some of the acid in a small boat was placed in a glass tube with a diameter of about 15 mm. One end of the tube was connected with a bottle containing a small quantity of sulphuric acid. The other end was connected with a cylinder which contained calcium chloride. By connecting this apparatus with a filter-pump, a current of dry air could be drawn through the tube. If the air was allowed to pass rapidly through the tube, the acid was decomposed when heated to about 128°. A white sublimate, which was very sweet, collected on the wall of the tube. If the current of air was shut off, the acid decomposed at 135° and white, transparent needles of pure benzoic sulphinide collected on the wall of the tube. Some of the needles were from 10 to 12 mm. in length. The acid contains no water of crystallization.

The acid crystallizes in white, opaque needles, if the solution is allowed to stand at least one week before crystallization takes place. The needles melt at 152°. The needles are more soluble in water than the plates. This form of the acid contains water of crystallization. Below 100° it lost just 0.5 molecule of water.

	Calculated for $C_6H_4\langle^{COOH}_{SO_2NH_2} + \frac{1}{2}H_2O$.	Found.
H_2O	4.29	4.28

When dissolved in alcohol, the needles crystallize from the solution in plates which melt at 152°. The needles decomposed when heated to about 115°, and a white sublimate collected on the walls of the tube. The sublimate was very sweet.

Ten grams of benzoic sulphinide were added to a caustic soda solution, which was prepared by dissolving 20 grams of caustic soda in 250 cc. of water. The solution was treated in the same way as the previous solution. After treating the solution with hydrochloric acid, if it is allowed to

stand over night, the acid crystallizes out in the form of needles. These proportions give nearly a quantitative yield of the acid in the form of needles.

A careful examination of the needles showed that they agreed in every respect with the needles obtained by the recrystallization of the plate acid from water. They melted at 152°. If the temperature is kept at 152° for a while, the acid is changed to a solid which melts at 215°. If heated in the apparatus previously described, the needles lose 0.5 molecule of water of crystallization below 100° C.

I. 0.3484 gram acid lost 0.0150 gram H_2O at 90°.
II. 0.2920 gram acid lost 0.0119 gram H_2O at 98°.

	Calculated for $C_6H_4\langle^{COOH}_{SO_2NH_2} + \frac{1}{2}H_2O$.	Found. I.	II.
H_2O	4.29	4.30	4.11

If a current of air was allowed to flow rapidly through the tube, the acid decomposed at 115° and was partially fused. When the current of air was cut off entirely, the acid decomposed at 145°. The acid was heated at this temperature for about six hours. During this time beautiful, transparent needles of pure benzoic sulphinide, some of which were several millimeters in length, collected on the walls of the tube. The needles were extremely sweet and melted at 223° to 224° (uncorrected). By taking proportions intermediate between the proportions used in the previous experiments (15 grams of sodium hydroxide with the same amount of benzoic sulphinide and water), a mixture is obtained which consists partly of the plate acid and partly of the needle acid. On account of the difference in solubility, they can easily be separated, the plates being less soluble than the needles.

All of the salts of orthosulphaminebenzoic acid crystallize from water solution in well-formed crystals. All of them contain water of crystallization with the exception of the monosilver, potassium, and ammonium salts. Without exception, they all become sweet when they lose their water of crystallization.

All the salts decompose at a few degrees above the temperature at which they give off their water of crystallization.

Sodium Orthosulphaminebenzoate, $C_6H_4\begin{cases}COONa\\SO_2NH_2\end{cases}$.—This salt crystallizes from an exceedingly concentrated water solution in fine, silky needles. Only a few needles were obtained from a solution which was allowed to stand several weeks in a small test-tube. Even then a slight disturbance of the tube would cause the needles to redissolve. As a general rule, the salt is deposited as a white, amorphous mass. The salt becomes sweet by simply exposing it to the air for a short while. The salt was dried (with drying-paper) and analyzed at once. The percentage of sodium agreed with 1.5 molecules of water and the percentage of water of crystallization agreed with 2.5 molecules of water.

I. 0.2114 gram salt lost 0.0357 gram H_2O below 110°.
II. 0.2210 gram salt lost 0.0375 gram H_2O below 110°.
III. 0.2628 gram salt lost 0.0442 gram H_2O below 110°.

	Calculated for $C_6H_4\begin{cases}COONa\\SO_2NH_2\end{cases} + 2\frac{1}{2}H_2O$.	Found. I.	II.	III.
H_2O	16.79	16.88	16.96	16.81

	Calculated for $C_6H_4\begin{cases}COONa\\SO_2NH_2\end{cases} + 1\frac{1}{2}H_2O$.	Found. I.	II.	III.
Na	9.20	9.10	9.12	9.11

A few of the needles were obtained and a determination of the sodium agreed with 2.5 molecules of water.

I. 0.0174 gram salt gave 0.0046 gram Na_2SO_4.
II. 0.1945 gram salt gave 0.0546 gram Na_2SO_4.

	Calculated for $C_6H_4\begin{cases}COONa\\SO_2NH_2\end{cases} + 2\frac{1}{2}H_2O$.	Found. I.	II.
Na	8.58	8.62	8.58

Potassium Orthosulphaminebenzoate, $C_6H_4\begin{cases}COOK\\SO_2NH_2\end{cases}$.—This salt is extremely soluble in water; insoluble in methyl alco-

hol. It is deposited from a water solution as a white, amorphous mass. It crystallizes from a mixture of alcohol and water in large, transparent plates.

I. 0.1445 gram salt gave 0.0528 gram K_2SO_4.
II. 0.1265 gram salt gave 0.0457 gram K_2SO_4.

	Calculated for $C_6H_4\langle^{COOK}_{SO_2NH_2}$	Found. I.	II.
K	16.32	16.33	16.20

Calcium Orthosulphaminebenzoate, $\left(C_6H_4\langle^{COO}_{SO_2NH_2}\right)_2Ca + 2H_2O$.—This crystallizes from a water solution in well-formed, transparent crystals.

If crystallization takes place at once, well-formed crystals are obtained; but if the solution is allowed to stand several days, the salt is deposited as a white, crystalline mass.

I. 0.5475 gram salt lost 0.0414 gram H_2O below 140°.
II. 0.3776 gram salt lost 0.0277 gram H_2O below 140°.
I. 0.2114 gram salt gave 0.0598 gram $CaSO_4$.
II. 0.2926 gram salt gave 0.0829 gram $CaSO_4$.

	Calculated for $\left(C_6H_4\langle^{COO}_{SO_2NH_2}\right)_2Ca + 2H_2O$.	Found. I.	II.
Ca	8.40	8.27	8.30
H_2O	7.56	7.57	7.33

Barium Orthosulphaminebenzoate, $\left(C_6H_4\langle^{COO}_{SO_2NH_2}\right)_2 + 3H_2O$.—This salt is quite soluble in water and fairly soluble in alcohol. It crystallizes from a water solution in transparent plates, and sometimes it crystallizes from a water solution in needles in the form of rosettes. It crystallizes in needles from alcohol solution. It agrees in every respect with the salt prepared by W. A. Noyes[1] with the exception of the number of molecules of water of crystallization. Noyes prepared two salts, one with 2

[1] *Loc. cit.*

molecules and another with 9 molecules of water of crystallization. This salt loses its water of crystallization when exposed to the air.

0.1823 gram salt lost 0.0171 gram H_2O below 150°.

I. 0.1214 gram salt gave 0.0483 gram $BaSO_4$.

II. 0.1076 gram salt gave 0.0426 gram $BaSO_4$.

	Calculated for $\left(C_6H_4\begin{matrix}COO\\SO_2NH_2\end{matrix}\right)_2Ba + 3H_2O$.	Found. I.	II.
Ba	23.18	23.39	23.32
H_2O	9.14	9.14	....

Strontium Orthosulphaminebenzoate, $\left(C_6H_4\begin{matrix}COO\\SO_2NH_2\end{matrix}\right)_2Sr + 2H_2O$.—If the solution is allowed to evaporate spontaneously, this salt crystallizes in long, transparent, needle-like crystals, some of which are 3 or 4 mm. in length. The crystals remain transparent when exposed to the air.

I. 0.2151 gram salt lost 0.0150 gram H_2O below 140°.

I. 0.1385 gram salt gave 0.0486 gram $SrSO_4$.

II. 0.2231 gram salt gave 0.0783 gram $SrSO_4$.

	Calculated for $\left(C_6H_4\begin{matrix}COO\\SO_2NH_2\end{matrix}\right)_2Sr + 2H_2O$.	Found. I.	II.
Sr	16.71	16.71	16.67
H_2O	6.87	6.97	....

Zinc Orthosulphaminebenzoate, $\left(C_6H_4\begin{matrix}COO\\SO_2NH_2\end{matrix}\right)_2Zn + 3H_2O$.—Two grams of the acid were dissolved in a sufficient quantity of water and pure zinc carbonate was added till the solution was neutral. The solution was evaporated to a slight extent, and allowed to stand in a desiccator over night. Short, opaque, needle-like crystals were deposited during the night. If the solution is allowed to evaporate spontaneously, after several days large, transparent, needle-like crystals are deposited, some of which were

from 1 to 2 cm. in length. The crystals do not lose their transparency when exposed to the air. The salt is fairly soluble in water.

I. 0.0809 gram salt lost 0.0081 gram H_2O below 130°.
II. 0.0690 gram salt lost 0.0070 gram H_2O below 130°.
I. 0.0449 gram salt gave 0.0137 gram $ZnSO_4$.
II. 0.0621 gram salt save 0.0192 gram $ZnSO_4$.
III. 0.1476 gram salt gave 0.0456 gram $ZnSO_4$.

	Calculated for $\left(C_6H_4\begin{matrix}COO\\SO_2NH_2\end{matrix}\right)_2Zn + 3H_2O$.	Found. I.	II.	III.
Zn	12.59	12.24	12.40	12.46
H_2O	10.39	10.01	10.15	....

The zinc salt was also prepared from the needle acid in order to compare it with the zinc salt prepared from the plate acid. The two salts resemble one another in every respect with one exception. The solution of the salt from the needle acid, when allowed to evaporate spontaneously, deposited large, opaque, needle-like crystals instead of the transparent needles obtained from the plate acid.

0.0652 gram salt gave 0.0201 gram $ZnSO_4$.
0.0138 gram salt lost 0.0138 gram H_2O below 150°.

	Calculated for $\left(C_6H_4\begin{matrix}COO\\SO_2NH_2\end{matrix}\right)_2Zn + 3H_2O$.	Found.
Zn	12.59	12.42
H_2O	10.39	10.64

Magnesium Orthosulphaminebenzoate, $\left(C_6H_4\begin{matrix}COO\\SO_2NH_2\end{matrix}\right)_2Mg + 4H_2O$.—This salt crystallizes in well-formed, transparent needles, which are deposited in the form of rosettes. It is extremely soluble in water.

I. 0.1850 gram salt lost 0.0270 gram below 175°.
II. 0.2458 gram salt lost 0.0355 gram H_2O below 175°.
I. 0.2129 gram salt gave 0.0519 gram $MgSO_4$.
II. 0.1726 gram salt gave 0.0425 gram $MgSO_4$.
III. 0.1416 gram salt gave 0.0341 gram $MgSO_4$.

	Calculated for $\left(C_6H_4\begin{matrix}COO\\SO_2NH_2\end{matrix}\right)_2Mg + 4H_2O$.	Found. I.	II.	III.
Mg	4.84	4.84	4.92	4.81
H_2O	14.52	14.59	14.42	....

Copper Orthosulphaminebenzoate, $\left(C_6H_4\begin{matrix}COO\\SO_2NH_2\end{matrix}\right)_2Cu + 3H_2O$.—This forms large, blue, feathery needles, some of which are more than a centimeter in length. The salt is insoluble in alcohol and very difficultly soluble in water. The salt turned a deep-green color when it lost its water of crystallization.

I. 0.1369 gram salt lost 0.0144 gram H_2O below 170°.
II. 0.0895 gram salt lost 0.0095 gram H_2O below 170°.
III. 0.0951 gram salt lost 0.0085 gram H_2O below 170°.
I. 0.1684 gram salt gave 0.0209 gram CuO.
II. 0.3018 gram salt gave 0.0456 gram CuO.

	Calculated for $\left(C_6H_4\begin{matrix}COO\\SO_2NH_2\end{matrix}\right)_2Cu + 3H_2O$.	Found. I.	II.
Cu	12.23	12.41	12.32
H_2O	10.44	10.51	10.91

Monosilver Orthosulphaminebenzoate.—This was prepared by neutralizing 2 grams of the acid with ammonium hydroxide, and then boiling the solution until no odor of ammonia could be detected. Silver nitrate was added to the solution until no further precipitation took place. By allowing the solution to stand over night, fine, feathery needles of a light-gray color were deposited. The salt is soluble in hot water, but insoluble in cold water. It becomes dark when exposed to the light. It resembles, in every respect, the salt prepared by Noyes[1] by the same method.

I. 0.0875 gram salt gave 0.0307 gram Ag.
II. 0.1171 gram salt gave 0.0412 gram Ag.

	Calculated for $C_6H_4\begin{matrix}COOAg\\SO_2NH_2\end{matrix}$.	Found. I.	II.
Ag	35.06	35.08	35.17

[1] *Loc. cit.*

Disilver Orthosulphaminebenzoate, $C_6H_4\begin{cases}CO_2Ag\\SO_2NHAg\end{cases} + H_2O$.—This was prepared by neutralizing about 2 grams of acid with ammonium hydroxide and then adding about three-fourths as much ammonium hydroxide in excess as was required to neutralize the solution. Silver nitrate was added until no further precipitation took place. The salt was deposited as a white, amorphous mass, which dissolves in boiling hot water. By allowing the solution to stand over night, the salt separated out in the form of silver-colored leaflets, which became dark when exposed to the light. This salt is much less soluble in water than the monosilver salt, and resembles in every respect, with one exception, the disilver salt prepared by Noyes[1] by treating the barium salt with silver nitrate. This salt contains 1 molecule of water of crystallization.

The salt was thoroughly dried and was allowed to remain wrapped in drying-paper for one week. It was then heated to 140° in the apparatus previously described. The current of air was cut off and water could be distinctly seen as it collected as drops in both ends of the tube. After losing its water, it becomes dark-brown in color.

I. 0.1231 gram salt lost 0.0053 gram H_2O at 167°.

I. 0.1867 gram salt gave 0.0933 gram Ag.

II. 0.1097 gram salt gave 0.0549 gram Ag.

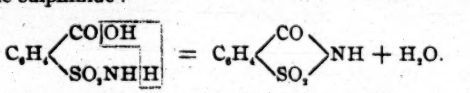
	Calculated for $C_6H_4\begin{cases}COOAg\\SO_2NHAg\end{cases} + H_2O$.	Found. I.	II.
Ag	49.88	49.97	50.04
H_2O	4.15	4.30	....

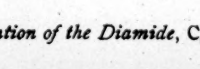
Ammonium Orthosulphaminebenzoate, $C_6H_4\begin{cases}COONH_4\\SO_2NH_2\end{cases}$.—This is quite soluble in water and crystallizes from a water solution in transparent plates. It contains no water of crystallization, but becomes very sweet when heated to 125°, and decomposes quite easily.

[1] *Loc. cit.*

Action of Phosphorus Oxychloride on the Sulphamine Acid.

Five grams of the acid were mixed with 5 grams of phosphorus oxychloride and heated on a water-bath for two hours. No chloride was formed. All of the acid was converted into benzoic sulphinide:



Preparation of the Diamide,  .

Ten grams of the acid were mixed with 6 grams of ammonium sulphocyanate. The mixture was heated, in a closed bath, for three days. During this time it was frequently stirred. As the acid is converted into benzoic sulphinide at quite a low temperature, the mixture was heated from 90° to 100° the first day, from 130° to 135° the second day, and from 150° to 160° the third day. The mass, which is of a light-brown color, is allowed to cool, when it becomes brittle. It is then pulverized and treated with boiling alcohol, in which it is soluble. After filtering, the solution is allowed to cool, when light-colored needles are deposited. Melting-point 263°.

Analyses gave the following results:

I. 0.1296 gram diamide gave 0.1528 gram $BaSO_4$.
I. 0.1565 gram diamide gave 0.0209 gram N.
II. 0.1413 gram diamide gave 0.0188 gram N.

	Calculated for	Found. I.	II.
S	16.00	16.20	....
N	14.00	13.35	13.27

I am indebted to Mr. C. E. Waters for the nitrogen determinations. He observed the fact that the ammonia is given off in two different stages. One portion of the ammonia was given off when the sodium hydroxide solution was dilute. After heating some time, the second portion was given off when the solution had become very concentrated.

Preparation of Orthocarbaminebenzenesulphonic Acid.

This acid was first prepared by Fahlberg and Barge[1] by the following method: Orthosulphobenzoic anhydride, when treated with ammonia, reacts according to this equation:

$$C_6H_4\begin{cases}CO\\SO_2\end{cases}O + 2NH_3 = C_6H_4\begin{cases}CONH_2\\SO_2ONH_4\end{cases}$$

The ammonium salt, when treated with silver nitrate, is easily converted into the silver salt. The free acid is obtained by treating the silver salt with sulphuric acid.

They describe the acid as crystallizing in thick, prismatic crystals, which are easily soluble in water and alcohol, and contain 1 molecule of water of crystallization. Melting-point 185° to 186° (uncorrected). By melting the acid with potassium hydroxide, ammonia is given off, but when simply heated no ammonia is given off.

The acid was prepared later by Jesurun[2] by heating orthocyanbenzenesulphone chloride with water or alcohol.

Karslake[3] also obtained the acid by hydrolysis of orthocyanbenzenesulphonic acid by means of dilute alkali:

$$C_6H_4\begin{cases}CN\\SO_2OH\end{cases} + H_2O = C_6H_4\begin{cases}CONH_2\\SO_2OH\end{cases}$$

The potassium salt of the acid can be obtained in any desired quantity by treating the acid potassium salt of orthosulphobenzoic acid with ammonium sulphocyanate.[4]

The substances were mixed together in the proportion of 5 parts of acid potassium salt to 3 parts of ammonium sulphocyanate. The mixture was heated in a closed bath for three days at a temperature of from 180° to 200° C. During this time it was occasionally stirred. The mass, which is of a brown color, is allowed to cool, when it becomes a stiff cake. It is then finely pulverized and digested with boiling alcohol several times. The potassium salt of the acid, which is in the

[1] Ber. d. chem. Ges., 22, 758.
[2] *Ibid.*, 26, 2288.
[3] Dissertation, Johns Hopkins University (1896), page 18.
[4] English Patent, Newton & Son, February 23, 1895.

form of sandy crystals, was separated from the alcohol by filtering. The salt, when recrystallized from water, separates out in large, transparent plates.

When the potassium salt is treated with silver nitrate in the proportion of their molecular weights, reaction takes place with the greatest ease with the formation of the silver salt of orthocarbaminebenzenesulphonic acid. The acid is obtained by treating the silver salt with hydrochloric acid. The acid crystallizes from a very concentrated water solution in large, thick, transparent crystals, which are quite soluble in alcohol. Melting-point 193° to 194° (uncorrected). The crystals remain transparent when exposed to the air. It does not become sweet when it loses its 1 molecule of water of crystallization, neither does it become sweet by continued heating. It decomposes when heated to 125°.

I. 0.2691 gram acid lost 0.0228 gram H_2O below 120°.
II. 0.2585 gram acid lost 0.0214 gram H_2O below 120°.

	Calculated for $C_6H_4\langle^{CONH_2}_{SO_3OH} + H_2O$.	Found. I.	II.
H_2O	8.22	8.47	8.27

The salts of this acid do not crystallize as well as the salts of orthosulphaminebenzoic acid, but are much more soluble in water. Most of the salts contain water of crystallization but they do not become sweet when they lose their water, neither do they become sweet when they are decomposed.

Potassium Orthocarbaminebenzenesulphonate, $C_6H_4\langle^{CONH_2}_{SO_3OK} + H_2O$.—This salt crystallizes from a water solution in large, transparent plates. It is quite soluble in water and in alcohol. It crystallizes from alcohol in needles. The salt is deliquescent. If the large, transparent crystals are placed in a beaker and covered with water, the moment they become warm a crackling sound can be distinctly heard some distance from the water-bath. The crystals become opaque and crumble to pieces. This phenomenon is doubt-

less due to the fact that the salt loses its water of crystallization very easily. In this instance it loses it under water.

A similar salt is described by Remsen and Karslake,[1] derived from cyanbenzenesulphonic acid, and by Sohon,[2] derived from the ammonium salt of benzaminesulphonic acid.

I. 0.3439 gram salt lost 0.0239 gram H_2O below 100°.
II. 0.5499 gram salt lost 0.0380 gram H_2O below 100°.
III. 0.4801 gram salt lost 0.0331 gram H_2O below 100°.
I. 0.4660 gram salt gave 0.1583 gram K_2SO_4.
II. 0.4904 gram salt gave 0.1657 gram K_2SO_4.
III. 0.4246 gram salt gave 0.1441 gram K_2SO_4.

	Calculated for $C_6H_4\langle^{CONH_2}_{SO_2OK} + H_2O$.	Found. I.	II.	III.
K	15.21	15.21	15.11	15.21
H_2O	7.00	6.94	6.91	6.89

Silver Orthocarbaminebenzenesulphonate, $C_6H_4\langle^{CONH_2}_{SO_2OAg} + H_2O$.—When the potassium salt of the carbamine acid in solution is treated with silver nitrate in the proportion of their molecular weights, the silver salt is formed. The salt which is fairly soluble in water crystallizes in large, monoclinic, transparent plates. It is decomposed when brought in contact with wet filter-paper and becomes dark when exposed to the light for any length of time.

This salt resembles in every respect the salt prepared by Fahlberg and Barge[3] by treating the ammonium salt of the carbamine acid with silver nitrate.

I. 0.3557 gram salt lost 0.0193 gram H_2O below 136°.
II. 0.4136 gram salt lost 0,0228 gram H_2O below 136°.
I. 0.2362 gram salt gave 0.0784 gram Ag.
II. 0.3681 gram salt gave 0.1215 gram Ag.

	Calculated for $C_6H_4\langle^{CONH_2}_{SO_2OAg} + H_2O$.	Found. I.	II.
Ag	33.14	13.19	33.00
H_2O	5.52	5.45	5.51

[1] This JOURNAL, 18, 825.
[2] *Ibid.*, 20, 270.
[3] Ber. d. chem. Ges., 22, 759.

Trisilver Orthocarbaminebenzenesulphonate, $C_6H_4\begin{cases}CONAg_2\\SO_2OAg\end{cases}$.—A small quantity of potassium orthocarbaminebenzenesulphonate was dissolved in water and 2 drops of ammonia were added to the solution. A hot solution of silver nitrate was added until no further precipitate was formed. The salt was deposited as a white, amorphous mass, which was insoluble in boiling water. The salt becomes dark when exposed to the light and is extremely stable. It was with the greatest difficulty that it was decomposed. Therefore, the following analysis cannot be reported with confidence:

	Calculated for $C_6H_4\begin{cases}CONAg_2\\SO_2OAg\end{cases}$	Found.
Ag	62.07	62.56

Sodium Orthocarbaminebenzenesulphonate, $C_6H_4\begin{cases}CONH_2\\SO_2ONa\end{cases} + 2H_2O$.—This salt was prepared by treating the silver salt with sodium chloride. It is quite soluble in water, from which solution it crystallizes in large, transparent plates, which belong to the monoclinic system.

This resembles in every respect the salt described by Remsen and Karslake.[1]

I. 0.1771 gram salt lost 0.0246 gram H_2O below 145°.
II. 0.1572 gram salt lost 0.0217 gram H_2O below 145°.
I. 0.1186 gram salt gave 0.0324 gram Na_2SO_4.
II. 0.0386 gram salt gave 0.0034 gram Na_2SO_4.

	Calculated for $C_6H_4\begin{cases}CONH_2\\SO_2ONa\end{cases} + 2H_2O$.	Found. I.	Found. II.
Na	8.88	8.85	8.80
H_2O	13.85	13.89	13.80

Barium Orthocarbaminebenzenesulphonate, $\left(C_6H_4\begin{cases}CONH_2\\SO_2O\end{cases}\right)_2Ba + 2H_2O$.—This salt was prepared by

[1] *Loc. cit.*

treating the silver salt with hydrochloric acid and then adding pure barium carbonate to the point of neutralization. The salt crystallized in transparent plates from a very concentrated water solution.

The percentage of water of crystallization agrees with 2 molecules of water. The percentage of barium agrees with 2.5 molecules of water. The following analyses were made of different portions of the salt prepared at different times:

I. 0.1787 gram salt lost 0.0114 gram H_2O below 175°.
II. 0.2194 gram salt lost 0.0138 gram H_2O below 175°.
I. 0.0887 gram salt gave 0.0357 gram $BaSO_4$.
II. 0.1584 gram salt gave 0.0637 gram $BaSO_4$.

	Calculated for $\left(C_6H_4\begin{matrix}CONH_2\\SO_2O\end{matrix}\right)_2Ba + 2H_2O$.	Found. I.	II.
H_2O	6.28	6.37	6.28

	Calculated for $\left(C_6H_4\begin{matrix}CONH_2\\SO_2O\end{matrix}\right)_2Ba + 2\frac{1}{2}H_2O$.	Found. I.	II.
Ba	23.54	23.66	23.61

Strontium Orthocarbaminebenzenesulphonate, $\left(C_6H_4\begin{matrix}CONH_2\\SO_2O\end{matrix}\right)_2Sr$.—This salt was prepared just as the corresponding barium salt by using strontium carbonate. The salt separated out of an extremely concentrated water solution in small, transparent crystals with no definite form.

I. 0.2145 gram salt gave 0.0815 gram $SrSO_4$.
II. 0.2017 gram salt gave 0.0764 gram $SrSO_4$.

	Calculated for $\left(C_6H_4\begin{matrix}CONH_2\\SO_2O\end{matrix}\right)_2Sr$.	Found. I.	II.
Sr	17.95	18.08	18.04

Calcium Orthocarbaminebenzenesulphonate, $\left(C_6H_4\begin{matrix}CONH_2\\SO_2O\end{matrix}\right)_2Ca + 2H_2O$.—This salt was prepared just as the corresponding strontium salt by using pure calcium

carbonate. The salt crystallized in large, transparent plates from a very concentrated water solution.

I. 0.1333 gram salt lost 0.0097 gram H_2O below 185°.
II. 0.1986 gram salt lost 0.0150 gram H_2O below 185°.
I. 0.1169 gram salt gave 0.0332 gram $CaSO_4$.
II. 0.1127 gram salt gave 0.0323 gram $CaSO_4$.

	Calculated for $\left(C_6H_4\begin{matrix}CONH_2\\SO_2O\end{matrix}\right)_2Ca + 2H_2O$.	Found. I.	II.
Ca	7.56	7.28	7.55
H_2O	8.40	8.29	8.43

Zinc Orthocarbaminebenzenesulphonate, $\left(C_6H_4\begin{matrix}CONH_2\\SO_2O\end{matrix}\right)_2Zn + 3H_2O$.—This salt was prepared by treating the acid with pure zinc carbonate. The salt is deposited from a very concentrated water solution in the form of short, thick needles. It is efflorescent.

I. 0.2187 gram salt lost 0.0227 gram H_2O below 150°.
II. 0.2477 gram salt lost 0.0256 gram H_2O below 150°.
I. 0.0934 gram salt gave 0.0286 gram $ZnSO_4$.
II. 0.1022 gram salt gave 0.0320 gram $ZnSO_4$.

	Calculated for $\left(C_6H_4\begin{matrix}CONH_2\\SO_2O\end{matrix}\right)_2 + 3H_2O$.	Found. I.	II.
Zn	12.59	12.31	12.62
H_2O	10.39	10.37	10.34

Magnesium Carbaminebenzenesulphonate, $\left(C_6H_4\begin{matrix}CONH_2\\SO_2O\end{matrix}\right)_2 + 2H_2O$.—This salt was prepared just as the zinc salt by using pure magnesium carbonate. The salt separates out as a crystalline mass from a very concentrated water solution.

I. 0.1983 gram salt lost 0.0146 gram H_2O below 140°.
II. 0.2002 gram salt lost 0.0158 gram H_2O below 140°.
I. 0.1204 gram salt gave 0.0310 gram $MgSO_4$.
II. 0.1904 gram salt gave 0.0490 gram $MgSO_4$.

	Calculated for $\left(C_6H_4\begin{matrix}CONH_2\\SO_3O\end{matrix}\right)_2Mg + 2H_2O$.	Found. I.	II.
Mg	5.22	5.14	5.14
H_2O	7.82	7.36	7.89

Copper Orthocarbaminebenzenesulphonate, $\left(C_6H_4\begin{matrix}CONH_2\\SO_3O\end{matrix}\right)_2Cu + 4H_2O$.—This salt was prepared by boiling the acid with copper oxide on a water-bath. When allowed to cool the salt was deposited in beautiful, deep-blue plates. When the salt loses its water of crystallization it becomes gray. If a small quantity of water is added to the gray salt, it becomes light-blue.

I. 0.1761 gram salt lost 0.0240 gram H_2O below 200°.
II. 0.1760 gram salt lost 0.0240 gram H_2O below 200°.
I. 0.1083 gram salt gave 0.0127 gram CuO.
II. 0.0435 gram salt gave 0.0064 gram CuO.

	Calculated for $\left(C_6H_4\begin{matrix}CONH_2\\SO_3O\end{matrix}\right)_2Cu + 4H_2O$.	Found.	
Cu	11.86	11.72	11.72
H_2O	13.45	13.62	13.63

Ammonium Orthocarbaminebenzenesulphonate, $C_6H_4\begin{matrix}CONH_2\\SO_3ONH_4\end{matrix}$.—This salt crystallizes from a concentrated water solution in large plates. One plate obtained was at least 2.5 cm. in length. After heating the salt up to 140° no sweet taste could be detected. It melts at 262° to 263° (uncorrected).

I. 0.1503 gram salt lost 0.0062 gram H_2O below 125°.
II. 0.1404 gram salt lost 0.0059 gram H_2O below 125°.
I. 0.1562 gram salt gave 0.1649 gram $BaSO_4$.

	Calculated for $C_6H_4\begin{matrix}CONH_2\\SO_3ONH_4\end{matrix} + 1\frac{1}{2}H_2O$.	Found. I.	II.
H_2O	3.96	4.12	4.20

	Calculated for $C_6H_4\langle^{CONH_2}_{SO_3ONH_4}$	Found.
S	14.67	14.46

This salt was prepared by Fahlberg and Barge[1] and described as crystallizing from alcohol in white needles, which melt at 225° to 226°. Jesurun[2] describes it as crystallizing from water in granular crystals containing 1 molecule of water of crystallization. Remsen and Karslake[3] describe the salt as crystallizing from a water solution in thin, transparent needles, which contain no water of crystallization and which melt at 219° to 220° (uncorrected).

Preparation of the Chloride, $C_6H_4\langle^{CONH_2}_{SO_2Cl}$.—Five grams of the potassium salt were mixed with 5 grams of phosphorus oxychloride in a small flask. The flask was attached to a return condenser, and then placed in a bath which contained boiling water. The mixture was heated for about half an hour. The white mass was pulverized in a mortar and treated with cold water. The orthocarbaminebenzenesulphone chloride, which remains in the form of a white, crystalline powder, insoluble in water, is filtered off. It was then thoroughly dried. It crystallized from chloroform in small, thick, opaque plates. Melting-point 63°.

0.1156 gram salt gave, by the Carius method, 0.0984 gram AgCl.

	Calculated for $C_6H_4\langle^{CONH_2}_{SO_2Cl}$	Found.
Cl	16.17	16.00

This experiment will be repeated, as it is somewhat doubtful whether the product obtained was the chloride of the carbamine acid.

Potassium Orthocyanbenzenesulphonate, $C_6H_4\langle^{CN}_{SO_3OK}$.—

[1] *Loc. cit.*
[2] *Loc. cit.*
[3] *Loc. cit.*

This was prepared by treating the potassium salt with phosphorus oxychloride, as in the previous experiment, only the mixture in this experiment was simply warmed in the water-bath. The whole of the potassium salt was converted into the cyan salt. It crystallizes from a moderately dilute water solution in small, transparent needles, radiating from a common center.

If the mixture of the potassium salt and phosphorus oxychloride is placed in a cold water-bath and then heated to the boiling temperature, the potassium salt will be partly converted into the chloride and partly into the cyan potassium salt.

This salt resembles in every respect the salt described by Remsen and Karslake,[1] derived from ammonium cyanbenzenesulphonate.

	Calculated for $C_6H_4\langle^{CN}_{SO_2OK}$	Found. I.	II.
K	17.67	17.67	17.71

A small portion of the chloride was placed in a beaker, which was then placed in a dish of cold water. The chloride was treated with a small quantity of an ordinary solution of ammonium hydroxide. The beaker was allowed to stand in the water for about three hours, the contents being stirred at frequent intervals.

It was then warmed on a water-bath for about half an hour. The solution was then filtered and a white, crystalline substance remained in the filter-paper. It was soluble only in boiling alcohol, from which solution it crystallized in small, opaque, monoclinic (?) plates. The substance did not melt when heated to the boiling-point of sulphuric acid. A sulphur determination was made by the Liebig method. Ammonia was given off when the substance was fused with potassium hydroxide, although not as freely as in the case of the diamide made from the sulphamine acid.

0.1203 gram substance gave 0.1506 gram $BaSO_4$.

[1] *Loc. cit.*

	Calculated for $C_6H_4\langle^{CONH_2}_{SO_2NH_2}$	Found.
S	16.00	17.20

Possibly the substance was not thoroughly oxidized when fused with potassium hydroxide or else is not the diamide.

A FURTHER INVESTIGATION OF THE ACTION OF PHENOLS AND ALCOHOLS ON THE CHLORIDES OF PARANITROORTHOSULPHOBENZOIC ACID.[1]

By Victor John Chambers.

Action of Phenols.

The action of phenol upon the chlorides of orthosulphobenzoic acid has been studied. Remsen and Saunders[2] used the mixed chlorides and the symmetrical chloride, Remsen and McKee[3] both the symmetrical and the unsymmetrical chlorides.

In every case, a diphenyl ester and a red coloring-matter, supposed to be a sulphonphthalein, were obtained. Humphreys[4] repeated the work of Remsen and McKee and showed that, besides the two substances referred to, a third substance was obtained if the temperature was kept down. This proved to be the orthosulphone chloride of phenyl benzoate.

Less work has been done on the action of phenols upon the chlorides of paranitroorthosulphobenzoic acid. Henderson[5] tried the action of various phenols on the symmetrical chloride and obtained, with phenol and ortho- and paracresols, results analogous to those of Remsen and McKee.

It was thought best, therefore, to make a comparative study of the action of phenols upon the symmetrical and the unsymmetrical chloride.

[1] From the author's dissertation submitted, June, 1901, to the Board of University Studies of the Johns Hopkins University, in conformity with the requirements for the degree of Doctor of Philosophy. The investigation was undertaken at the suggestion of Professor Remsen and carried out under his guidance.

[2] This Journal, 17, 352.

[3] *Ibid.*, 18, 794.

[4] *Ibid.*, 30, 292.

[5] *Ibid.*, 25, 1.

The method in general use was to mix a few grams of the chloride with slightly more than the required amount of the phenol, and to heat this mixture in a test-tube immersed in a bath of sulphuric acid. A large amount of the phthalein is formed in this way, which makes the product very difficult of purification. Humphreys showed that the Schotten-Baumann reaction could be applied to this case. He heated a mixture of the chloride and the phenol in a beaker until it liquefied. A cold, dilute solution of potassium hydroxide was then added and the oily mass stirred occasionally until it solidified. After washing and crystallization from glacial acetic acid, a very clean, pure product was obtained.

Both these methods were used by the author. In some cases where they did not give good results a third, or rather a modification of the second method, was used. This consisted in adding an alcoholic solution of potassium hydroxide to an alcoholic solution of the mixture of chloride and phenol. Potassium chloride separated and the product was obtained from the solution either by adding water slowly or by evaporating alcohol. In some cases, where the product was but slightly soluble in alcohol, it separated with the potassium chloride. After thorough washing with water, it was crystallized from glacial acetic acid.

Action of Phenol upon the Symmetrical Chloride.—Three grams of the symmetrical chloride were mixed with slightly more than the calculated amount of phenol and heated in a test-tube in the acid-bath to 135°. The results obtained were similar to those described by Henderson. The product was the diphenyl ester melting at 118° to 119°. Humphreys[1] obtained both the diphenyl ester and a small amount of the orthosulphone chloride of phenyl benzoate by a similar treatment of the symmetrical chloride of orthosulphobenzoic acid. The product in this case was examined for the corresponding orthosulphone chloride, but none was discovered.

A small portion of symmetrical chloride was mixed with an excess of phenol and heated in a beaker until it melted. Dilute solution of potassium hydroxide was then added and

[1] *Loc. cit.*

the oily mass stirred until it solidified and crumbled. The time required varies with the strength of the alkali solution and the temperature. If the solution is moderately strong and the mixture heated on a water-bath, the action is over in five minutes. The crumbly mass was filtered off, washed, and crystallized from glacial acetic acid or alcohol. Beautiful needles of the diphenyl ester were obtained. Melting-point 118°.

A small portion of the symmetrical chloride and the necessary amount of phenol were dissolved in alcohol. To this solution was added an alcoholic solution of potassium hydroxide until precipitation of potassium chloride had ceased. Impure diphenyl ester was obtained from the solution. After recrystallization from glacial acetic acid, it melted at 118°.

Conduct of the Diphenyl Ester towards Reagents.—Dilute potassium hydroxide completely saponifies the diphenyl ester. Alcohol does not change it even when boiled for hours.

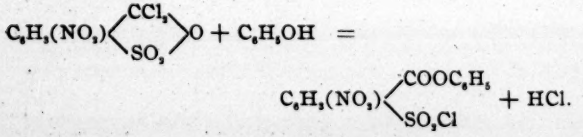
Action of Phenol upon the Unsymmetrical Chloride.—Three grams of the unsymmetrical chloride were mixed with a slight excess of phenol in a test-tube which was placed in a sulphuric acid-bath. Heat was applied and the temperature raised slowly to 135°, where it was kept for four hours. As soon as the substances melted, a red color was developed, which increased in depth until it became almost black. Hydrochloric acid commenced to come off at almost 100°. The rapidity of the evolution increased as the temperature rose, and decreased again after heating a short time at 135°. The black mass became somewhat viscous but did not harden on cooling. The cooled mass was treated with water, which dissolved much of the coloring-matter and caused the mass to harden.

The red solution so obtained was turned deep purple by the addition of an alkali. After as much of the coloring-matter had been extracted in this way as possible, the crumbly mass was decanted upon a filter and washed first with dilute alkali and then with hot water. The residue was recrystallized several times from glacial acetic acid. Light-brown, heavy needles were obtained which melted poorly at 145° to 147°.

These proved to be the paranitroorthosulphone chloride of phenyl benzoate.

The question arose whether any diphenyl ester was formed by this process. Humphreys,[1] working with the unsymmetrical chloride of orthosulphobenzoic acid, had obtained both products, the amount of each depending on the temperature. He found that, working at the lowest temperature at which the reaction would take place, he got a mixture containing, besides the phenyl ester chloride, a little of the diphenyl ester, while, if the temperature was raised, more diphenyl ester was found until, at a temperature just below the decomposition-point, practically only diphenyl ester was formed. This change is easily understood when it is borne in mind that the phenyl ester chloride itself reacts with phenol, forming the diphenyl ester. No diphenyl ester was found in the product of the reaction between phenol and the unsymmetrical chloride of paranitroorthosulphobenzoic acid. It will be shown later that the paranitroorthosulphone chloride of phenyl benzoate or, as it is often called, the phenyl ester chloride, does not react with phenol even when heated to the highest temperature short of decomposition.

A few grams of the unsymmetrical chloride were melted with an excess of phenol. The beaker was placed on ice, and to the oily mass was added a cold dilute solution of potassium hydroxide. The mass solidified very slowly. After washing and crystallizing from glacial acetic acid, pure crystals of phenyl ester chloride were obtained which melted at 146°. It is necessary to keep the temperature of the reaction low and the alkaline solution weak, for, if not, some or only diphenyl ester is obtained:



Analysis of the substance gave the following results:

[1] *Loc. cit.*

0.2662 gram substance gave 0.4465 gram CO_2 and 0.0660 gram H_2O.

0.3147 gram substance gave 0.1308 gram AgCl.

0.2746 gram substance gave 0.1108 gram AgCl.

0.3560 gram substance gave 0.0146 gram N.

	Calculated for $C_6H_3(NO_2)\langle^{COOC_6H_5}_{SO_2Cl}$	Found.
C	45.68	45.76
H	2.74	2.34
Cl	10.37	10.28
N	4.10	4.10

Decompositions of the Paranitroorthosulphone Chloride of Phenyl Benzoate.—When boiled with dilute *hyarochloric acid*, the chloride is completely saponified giving free paranitroorthosulphobenzoic acid.

When boiled with *water*, it gives two products, the free acid and its monophenyl ester, $C_6H_3\langle^{COOC_6H_5}_{SO_2OH}$. The ester was not obtained in pure condition but was identified by its crystalline form and an analysis.

Barium hydroxide gave results similar to those obtained by Humphreys.[1] The chloride was partly converted into the barium salt of paranitroorthosulphobenzoic acid and partly, apparently, into the diphenyl ester, the formation of which must be due to the action of the barium phenolate, first formed, upon some of the unchanged chloride:

$$\text{I. } 2C_6H_3(NO_2)\langle^{COOC_6H_5}_{SO_2Cl} + 4Ba(OH)_2 =$$

$$2C_6H_3(NO_2)\langle^{COO}_{SO_2O}\rangle Ba + (C_6H_5O)_2Ba + BaCl_2 + 4H_2O;$$

$$\text{II. } 2C_6H_3(NO_2)\langle^{COOC_6H_5}_{SO_2Cl} + (C_6H_5O)_2Ba =$$

$$2C_6H_3(NO_2)\langle^{COOC_6H_5}_{SO_2OC_6H_5} + BaCl_2.$$

[1] *Loc. cit.*

Ammonia gives nitrobenzoic sulphinide and the diphenyl ester, whether used in dilute or concentrated form.

Aniline gives the anil described by Remsen and Gray.[1]

Alcohols convert the chloride into the monophenyl ester.

Barium Phenyl Paranitroorthosulphobenzoate, $C_6H_3(NO_2)\begin{cases}COOC_6H_5\\SO_2O\end{cases}{}_2Ba + 5H_2O$. — This crystallizes from hot water in thin, lustrous plates. Another salt, containing probably 6 molecules of water, is formed when the hot solution is allowed to cool slowly. It has the form of white knobs.

0.2383 gram of the plates lost 0.024 gram H_2O at 170°.

0.2134 gram dried salt gave 0.0635 gram $BaSO_4$.

	Calculated for $\left(C_6H_3(NO_2)\begin{cases}COOC_6H_5\\SO_2O\end{cases}\right)_2Ba + 5H_2O$.	Found.
H_2O	10.34	10.41
	Calculated for anhydrous salt.	Found.
Ba	17.58	17.51

Potassium Phenyl Paranitroorthosulphobenzoate, $C_6H_3(NO_2)\begin{cases}COOC_6H_5\\SO_2OK\end{cases}$.—This crystallizes in somewhat heavy needles.

0.2549 gram salt gave 0.0610 gram K_2SO_4.

	Calculated for $C_6H_3(NO_2)\begin{cases}COOC_6H_5\\SO_2OK\end{cases}$	Found.
K	10.80	10.74

When the sulphone chloride is heated with phenol, even to the point at which decomposition begins, no diphenyl ester is formed. But when the two substances in alcoholic solution are treated with alcoholic potash, diphenyl ester is formed.

Action of Orthocresol upon the Symmetrical Chloride.—The results obtained by the heating together of these two sub-

[1] This JOURNAL, 19, 496.

stances were in perfect accord with those obtained by Henderson.[1]

Equal parts of the chloride and orthocresol were melted together. Dilute solution of potassium hydroxide was added and the mass stirred occasionally. The oily mass did not solidify perfectly even after two days' standing. It was dissolved in glacial acetic acid, from which solution rosettes of small crystals were obtained, melting at 95° to 97°. They were probably impure crystals of the unchanged chloride.

An alcoholic solution of potassium hydroxide was added slowly to an alcoholic solution of equal parts of the chloride and orthocresol. Granular crystals of potassium chloride at once separated. On allowing the alcoholic solution to evaporate, a crystalline mass was obtained that gave, upon recrystallization from glacial acetic acid, heavy needles melting at 90°.

This substance must be the same as was obtained in small quantity by Henderson by the fusion method. No analysis was made by him or the author, but there is little doubt that it is the diorthocresyl ester of paranitroorthosulphobenzoic acid.

Action of Orthocresol upon the Unsymmetrical Chloride.—The phenomena observed when these two substances were heated together were about the same as when the symmetrical chloride was used. Evolution of hydrochloric acid began a few degrees lower and the product did not become so hard on cooling. A much larger residue was left after washing which, when crystallized from glacial acetic acid, gave small, dark plates, melting poorly at 148°.

The Schotten-Baumann method gave better results. The mass hardened slowly and gave pure, white plates melting at 150° when crystallized from glacial acetic acid. These proved to be the paranitroorthosulphone chloride of orthocresylbenzoate.

0.3237 gram substance gave 0.5647 gram CO_2 and 0.0916 gram H_2O.

0.3456 gram substance gave 0.1365 gram AgCl.

[1] *Loc. cit.*

	Calculated for $C_6H_3(NO_2)\langle^{COOC_7H_7}_{SO_2Cl}$	Found.
C	47.26	47.57
H	2.81	3.29
Cl	9.96	9.74

Action of Paracresol upon the Symmetrical Chloride.—Equal parts of the symmetrical chloride and paracresol were melted together in a sulphuric acid-bath. A red color was developed quickly and deepened as the temperature rose. Hydrochloric acid came off at 100°. The temperature was raised to 115° and kept there for four hours, after which the mass was treated with cold water. It soon hardened, and after washing as before and recrystallizing from glacial acetic acid, short, thick needles were obtained which melted rather badly at 116°.

Equal parts of the symmetrical chloride and paracresol were melted together and treated with a 5 per cent solution of potassium hydroxide. The mass became oily, but hardened after two days. After washing and crystallizing from glacial acetic acid, fine, heavy needles were obtained, melting at 118°. The substance was the diparacresyl ester of paranitroorthosulphobenzoic acid obtained by Henderson[1] by the first of the two above processes.

Action of Paracresol upon the Unsymmetrical Chloride.—The reaction was carried on in the same way as with the symmetrical chloride. Hydrochloric acid was given off at about 100° and the mass turned from reddish-brown to black. The resultant mass, on washing and crystallization, gave small needles or prisms, melting at 152° (uncorrected). The product proved to be the paranitroorthosulphone chloride of paracresyl benzoate. The yield by this reaction is poor and hard to purify, yet it proved to be the only method by which it could be prepared.

The Schotten-Baumann method did not work smoothly in this case, the product being in every case the diparacresyl ester of paranitroorthosulphobenzoic acid. The reaction could

[1] *Loc. cit.*

not be made to stop half-way as it did with phenol and orthocresol.

That the product was the paranitroorthosulphone chloride of paracresyl benzoate was shown by the analysis:

0.2235 gram substance gave 0.3921 gram CO_2 and 0.0696 gram H_2O.

0.2571 gram substance gave 0.1005 gram AgCl.

	Calculated for $C_6H_3(NO_2)\langle^{COOC_7H_7}_{SO_2Cl}$.	Found.
C	47.26	47.87
H	2.81	3.45
Cl	9.96	9.71

Action of Orthonitrophenol upon the Symmetrical Chloride.—Equal parts of the phenol and the chloride were melted together and heated with a dilute solution of potassium hydroxide. The oil so formed solidified after five hours' standing to a crumbly mass that, on washing and crystallization from glacial acetic acid, gave fine needles, melting sharply at 164°. This substance proved to be the dinitrophenylester of paranitroorthosulphobenzoic acid, as the following analysis shows:

0.1665 gram substance gave 0.2822 gram CO_2 and 0.0428 gram H_2O.

0.3058 gram substance gave 0.0261 gram N.

	Calculated for $C_6H_3(NO_2)\langle^{COOC_6H_4NO_2}_{SO_2OC_6H_4NO_2}$	Found.
C	46.62	46.25
H	2.05	2.81
N	8.59	8.52

Action of Orthonitrophenol upon the Unsymmetrical Chloride.—When the chloride and phenol were heated together at 100°, the evolution of hydrochloric acid was slow. Even after heating to 125° for five hours, there was still some acid coming off. The mass was brown and was still an oil that hardened but partially on cooling. Caustic soda solution turned it to a crumbly mass after about two days' standing. The mass was washed and crystallized as usual. The product was an im-

pure dinitrophenyl ester. The Schotten-Baumann method worked very smoothly, the result being rosettes of fine needles that melted sharply at 164°. The action here evidently led to the diorthonitrophenyl ester. All attempts to get the ortho-sulphone chloride by modifying the conditions of the experiment were useless.

Action of Paranitrophenol upon the Symmetrical Chloride.—The reaction in this case was more vigorous than that between the orthonitrophenol and the chloride. After heating in an acid-bath for five hours at 125°, a hard, black mass was obtained that dissolved in a solution of caustic soda, but was reprecipitated by acids as a flocculent, chocolate-colored mass. It was not further investigated. No ethereal salt was obtained.

The Schotten-Baumann method worked smoothly, giving rosettes of thick needles, melting at 152°.

The modified Schotten-Baumann method also gave a good yield and a very pure product.

0.1514 gram substance gave 0.2606 gram CO_2 and 0.0447 gram H_2O.

	Calculated for $C_6H_3(NO_2)\langle^{COOC_6H_4NO_2}_{SO_2OC_6H_4NO_2}$	Found.
C	46.62	46.93
H	2.05	....

Action of Paranitrophenol upon the Unsymmetrical Chloride.—The only difference noticeable between the action of the unsymmetrical chloride and that of the symmetrical was that the unsymmetrical acted a little more readily when fused with the nitrophenol in the acid-bath.

Action of Resorcinol upon the Symmetrical Chloride.—The addition of alcoholic potassium hydroxide solution to an alcoholic solution of resorcinol and chloride gave a flocculent precipitate at once. When the alkaline solution was added, a red color was developed at first, but disappeared on stirring, if the alkaline solution was not in excess. As soon as the color persisted, even after vigorously stirring, the precipitate was

filtered off, washed thoroughly with water and alcohol, and dried.

The resulting, nearly colorless powder was practically insoluble in water, alcohol, glacial acetic acid, ether, chloroform, acetone, or ligroin. The very little that did dissolve in some of these solvents came out again in an amorphous condition. It was readily soluble in caustic alkalies, and was reprecipitated on acidifying. If, in the preparation of the substance, more alkali is added after the color has appeared, the precipitate dissolves, forming a reddish-green solution. This substance needs further investigation.

Action of Resorcinol upon the Unsymmetrical Chloride.—The action in this case was, in the main, the same as with the symmetrical chloride, the only difference being that the action took place a little more readily. The same hard mass was obtained which dissolved in alkaline solution and was reprecipitated by acids.

Action of Hydroquinol upon the Symmetrical Chloride.—When the modified Schotten-Baumann method was used, reaction took place as with resorcinol. The product had similar properties; in fact, what has been said about resorcinol can be repeated about the action of the chloride with hydroquinol.

Action of Hydroquinol upon the Unsymmetrical Chloride.—Hydrochloric acid commenced to come off at 120°, the melt becoming dark in color and viscous. After heating to 140° for four hours, a black mass was obtained which hardened on cooling, and acted like the mixture obtained with the other chloride.

In another experiment the temperature was kept at 125° for two hours. The mass darkened and thickened somewhat. When a solution of caustic soda was added, a part dissolved to a reddish-brown solution and the rest became oily, hardening only on standing. Nothing could be obtained from this mass but unchanged chloride.

Action of β-Naphthol upon the Symmetrical Chloride.—An alcoholic solution of potassium hydroxide was added to a

similar solution of chloride and β-naphthol. A flocculent precipitate at once separated, which collected in a gummy mass on stirring. The addition of alkali was stopped as soon as the pale-brown color produced by it became permanent. The gummy mass became hard on standing. It was then filtered off, washed with water and dilute alkali, and crystallized from glacial acetic acid. Beautiful, white needles were obtained; melting-point 134°. Analysis showed it to be the di-β-naphthyl ester of paranitroorthosulphobenzoic acid.

0.2553 gram substance gave 0.6017 gram CO_2 and 0.0908 gram H_2O.

	Calculated for $C_6H_3(NO_2)\langle^{COOC_{10}H_7}_{SO_3OC_{10}H_7}$	Found.
C	64.91	64.30
K	3.42	3.97

Action of β-Naphthol upon the Unsymmetrical Chloride.—The results in this case were wholly unsatisfactory. The Schotten-Baumann reaction could not be used in alcoholic solution because alcohol acts upon this chloride.

Action of Paraminophenol upon the Unsymmetrical Chloride.—Equal parts of the phenol and chloride were heated in the acid-bath. No action took place until 125° was reached, when a slight evolution of hydrochloric acid was observed. The temperature was kept at 120° for four hours, during which time vapors of hydrochloric acid came off slowly and the mass became black and sticky, but did not at any time become a fluid. On cooling, a hard, shining, brittle mass was obtained which was insoluble in water but easily soluble in a warm solution of caustic soda. The solution thus formed was black. On acidifying, a chocolate-colored precipitate was formed. No ethereal salt was obtained.

The Action of Phenol in Solution in Ammonia upon the Two Chlorides of Paranitroorthosulphobenzoic Acid.—Two grams of the symmetrical chloride were melted with an equal quantity of phenol and covered with dilute ammonia. The oily mass hardened very slowly. After two days' standing, the mass was well washed, then dissolved in hot alcohol. On cooling,

needle-shaped crystals separated that proved to be the diphenyl ester of paranitroorthosulphobenzoic acid. The alcoholic filtrate was allowed to evaporate at the room temperature and finally gave heavy prisms resembling the unchanged chloride, but melting at 135°. Analysis showed them to be phenyl paranitroorthosulphaminebenzoate.

The course of the experiment was varied in many ways but the result was always the same. The reaction is represented thus:

$$2C_6H_3(NO_2)\begin{cases}COCl\\SO_2Cl\end{cases} + 3C_6H_5OH + 5NH_3 =$$

$$C_6H_3(NO_2)\begin{cases}COOC_6H_5\\SO_2OC_6H_5\end{cases} + C_6H_3(NO_2)\begin{cases}COOC_6H_5\\SO_2NH_2\end{cases} + 4NH_4Cl.$$

0.3221 gram substance gave 0.5754 gram CO_2 and 0.0993 gram H_2O.

0.2366 gram substance gave 0.0204 gram N.

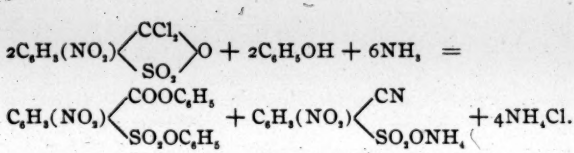
0.5172 gram substance gave 0.0445 gram N.

	Calculated for $C_6H_3(NO_2)\begin{cases}COOC_6H_5\\SO_2NH_2\end{cases}$	Found. I.	II.
C	48.45	48.71	....
H	3.10	3.42	....
N	8.69	8.62	8.61

The action of phenol and ammonia was tried also upon the unsymmetrical chloride. Equal parts of the unsymmetrical chloride and phenol were melted together and treated with dilute ammonia.

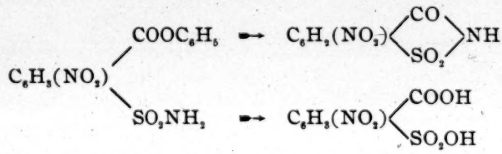
The oily mass soon solidified. It was then washed and dissolved in alcohol. Crystals of the diphenyl ester separated as in the previous experiment, but the alcoholic solution did not give any sulphonamide on evaporation. As Remsen and Gray[1] have shown that the action of ammonia upon the unsymmetrical chloride is to form the ammonium salt of paranitrocyanbenzenesulphonic acid, it is likely that some of this substance was also formed in this experiment.

[1] *Loc. cit.*



The action of caustic alkalies, ammonia, or water is the same as that of the same reagents upon the orthosulphonamide of phenyl benzoate.

A weak solution of potassium hydroxide causes the formation of the potassium salt of nitrobenzoic sulphinide. If the sulphonamide is heated a few moments with strong alkali, then acidulated, characteristic crystals of the acid potassium salt of paranitroorthosulphobenzoic acid are observed.



The action of ammonia was very slow. When the boiling was continued for five or more hours, the reaction was complete and nitrobenzoic sulphinide was formed.

The action of water was slower. This experiment was continued for five days without complete change taking place. There was some action, however, as the solution became gradually more bitter and gave more of a precipitate with bromine water. The common product of the action of weak alkalies, ammonia, and water upon the paranitroorthosulphonamide of phenyl benzoate is nitrobenzoic sulphinide.

Action of Alcohols upon the Chlorides.—Kastle[1] first studied the action of alcohols upon the chlorides of paranitroorthosulphobenzoic acid. He worked with the product of the reaction of phosphorus pentachloride upon the acid potassium salt of paranitroorthosulphobenzoic acid, a substance which was then supposed to be a chemical individual. He found that the substance dissolved readily in methyl alcohol with

[1] *Loc. cit.*

evolution of heat and, upon cooling, beautiful crystals were obtained.

This substance proved to be the paranitroorthosulphone chloride of methyl benzoate. If, however, the alcoholic solution of the chloride was boiled for a time, it became acid, and this acid was shown to be the acid methyl ester of paranitroorthosulphobenzoic acid. The sulphone chloride was also changed to the acid ester by boiling with alcohol.

The following equations represent these reactions :

1. $C_6H_3(NO_2)\begin{cases}COCl\\SO_2Cl\end{cases} + HOCH_3 =$

$$C_6H_3(NO_2)\begin{cases}COOCH_3\\SO_2Cl\end{cases} + HCl;$$

2. $C_6H_3(NO_2)\begin{cases}COOCH_3\\SO_2Cl\end{cases} + HOCH_3 =$

$$C_6H_3(NO_2)\begin{cases}COOCH_3\\SO_2OCH_3\end{cases} + HCl;$$

3. $C_6H_3(NO_2)\begin{cases}COOCH_3\\SO_2OCH_3\end{cases} + HOCH_3 =$

$$C_6H_3(NO_2)\begin{cases}COOCH_3\\SO_2OH\end{cases} + (CH_3)O.$$

Henderson[1] has studied the action of alcohols upon the symmetrical chloride. He found that when that chloride was dissolved in methyl alcohol and then cooled, no sulphone chloride came out. Any substance that did separate proved to be the unchanged chloride. If the alcoholic solution was boiled for a time the acid methyl ester described by Kastle was obtained. Ethyl alcohol acted in an analogous way. He modified the conditions of the experiment in various ways, but failed entirely to get the sulphone chloride from the symmetrical chloride. A small quantity of the unsymmetrical chloride that he had in his possession did give, with ethyl

[1] *Loc. cit.*

alcohol, a substance melting at 68° and corresponding to the sulphone chloride described by Kastle.

It was thought best to study now the action of alcohols upon the unsymmetrical chloride to see if the results explained the formation of the sulphone chlorides from the mixed chlorides.

Action of Methyl Alcohol upon the Unsymmetrical Chloride.—A small portion of the chloride was added to a little methyl alcohol. It dissolved readily. On putting the solution on ice, there was a rapid separation of crystals. These were filtered off and recrystallized from a little methyl alcohol. Small, thick prisms were obtained, melting at 82°.[1] This substance is the paranitrosulphone chloride of methyl benzoate,

$$C_6H_3(NO_2)\begin{cases}COOCH_3\\SO_2Cl\end{cases}.$$

When the chloride is boiled with alcohol for a short time, an acid solution is obtained that does not become cloudy on the addition of water. The alcoholic solution evaporates to a syrup, which finally solidifies to a crystalline mass. The compound was identified by means of the following salts and proved to be monomethyl paranitroorthosulphobenzoate.

Sodium Methyl Paranitroorthosulphobenzoate,

$$C_6H_3(NO_2)\begin{cases}COOCH_3\\SO_2ONa\end{cases}.$$—This crystallizes from a concentrated solution in transparent plates.

0.1955 gram substance, heated to 170°, lost 0.0003 gram.

0.1952 gram substance gave 0.0488 gram Na_2SO_4.

	Calculated for $C_6H_3(NO_2)\begin{cases}COOCH_3\\SO_2ONa\end{cases}$	Found.
Na	8.12	8.13

Potassium Methyl Paranitroorthosulphobenzoate,

$$C_6H_3(NO_2)\begin{cases}COOCH_3\\SO_2OK\end{cases}.$$—This is fairly soluble in cold water, from which it crystallizes in beautiful, iridescent plates.

[1] Kastle: This JOURNAL, II, 182.

I. 0.1238 gram substance gave 0.0370 gram K_2SO_4.
II. 0.1604 gram substance gave 0.0473 gram K_2SO_4.

	Calculated for $C_6H_3(NO_2)\langle^{COOCH_3}_{SO_2OK}$	Found. I.	II.
K	13.18	13.39	13.21

Action of Ethyl Alcohol upon the Unsymmetrical Chloride.—This substance was made by dissolving the unsymmetrical chloride in ethyl alcohol and cooling the solution. Beautiful, white, heavy needles separated at once. On recrystallization from ethyl alcohol, they melted sharply at 68°. The substance is the paranitrosulphone chloride of ethyl benzoate,

$$C_6H_3(NO_2)\langle^{COOC_2H_5}_{SO_2Cl}.$$

By boiling the unsymmetrical chloride with alcohol until a small portion dissolved in water to a clear solution, a very acid solution could be obtained which evaporated to a syrup without crystallizing. On long standing, however, this syrup did solidify to a crystalline mass.

The acid is also obtained by dissolving the unsymmetrical chloride in more alcohol than is necessary to keep the above sulphone chloride in solution, and allowing this solution to evaporate at the room temperature.

Barium Ethyl Paranitroorthosulphobenzoate,

$$\left(C_6H_3(NO_2)\langle^{COOC_2H_5}_{SO_2O}\right)_2Ba + 4H_2O.$$

—This salt crystallizes in long, white needles. It was recrystallized several times. The salt is very soluble in hot water, but only slightly in cold.

0.2549 gram substance lost, by heating to 170°, 0.0238 gram H_2O.

0.2311 gram substance gave 0.0786 gram $BaSO_4$.

	Calculated for $\left(C_6H_3(NO_2)\langle^{COOC_2H_5}_{SO_2O}\right)_2Ba + 4H_2O$.	Found.
H_2O	9.51	9.34

	Calculated for the dry salt.	Found.
Ba	20.00	20.02

Potassium Ethyl Paranitroorthosulphobenzoate, $C_6H_3(NO_2)\begin{cases}COOC_2H_5\\SO_2OK\end{cases} + H_2O$.—This salt is very soluble in water and crystallizes from a concentrated solution in short, heavy prisms.

0.2763 gram substance lost, by heating to 170° C., 0.0150 gram H_2O.

0.2458 gram dried salt gave 0.0699 gram K_2SO_4.

	Calculated for $C_6H_3(NO_2)\begin{cases}COOC_2H_5\\SO_2OK\end{cases} + H_2O$.	Found.
H_2O	5.42	5.43
	Calculated for dry salt.	Found.
K	12.59	12.75

Action of Propyl Alcohol upon the Unsymmetrical Chloride.—A portion of the unsymmetrical chloride was dissolved in warm propyl alcohol. Upon cooling, large, thin plates of the paranitrosulphone chloride of propyl benzoate,

$$C_6H_3(NO_2)\begin{cases}COOC_3H_7\\SO_2Cl\end{cases},$$

separated. After recrystallization from warm propyl alcohol, the substance melted at 76°.

I. 0.3273 gram substance gave 0.1523 gram AgCl.

II. 0.2743 gram substance gave 0.1276 gram AgCl.

	Calculated for $C_6H_3(NO_2)\begin{cases}COOC_3H_7\\SO_2Cl\end{cases}$.	Found. I.	Found. II.
Cl	11.51	11.50	11.51

By boiling the unsymmetrical chloride with propyl alcohol in a flask, connected with a return condenser, until a solution was obtained that did not turn cloudy with water, then evaporating to a syrup and adding water, it gave a clear, very acid solution that decomposed carbonates readily. By the aid of the salts below described, the acid was shown to be the monopropyl ester of paranitroorthosulphobenzoic acid,

$$C_6H_3(NO_2)\begin{cases}COOC_3H_7\\SO_2OH\end{cases}.$$

Barium propyl paranitroorthosulphobenzoate,

$\left(C_6H_3(NO_2)\begin{cases}COOC_3H_7\\SO_2O\end{cases}\right)_2Ba + 4H_2O$, crystallizes well from warm water in long needles with a somewhat greenish hue. The crystals are easily soluble in warm water, less so in cold. They contain 4 molecules of water of crystallization, which are driven off below 170°.

0.2337 gram substance lost 0.0219 gram on heating to 170°.
0.2118 gram of dried salt gave 0.0689 gram $BaSO_4$.

	Calculated for $\left(C_6H_3(NO_2)\begin{cases}COOC_3H_7\\SO_2O\end{cases}\right)_2Ba + 4H_2O$.	Found.
H_2O	9.17	9.37
	Calculated for dry salt.	Found.
Ba	19.26	19.15

Potassium propyl paranitroorthosulphobenzoate,

$C_6H_3(NO_2)\begin{cases}COOC_3H_7\\SO_2OK\end{cases}$, crystallizes from a concentrated solution in small, heavy needles. It is easily soluble in both hot and cold water.

0.1750 gram substance lost nothing on heating to 170°.
0.1750 gram substance gave 0.0471 gram K_2SO_4.

	Calculated for $C_6H_3(NO_2)\begin{cases}COOC_3H_7\\SO_2OK\end{cases}$.	Found.
K	11.92	12.06

The results just described, taken with those of Henderson on the action of alcohols upon the symmetrical chloride, explain more fully the results obtained by Kastle. The sulphone chloride that he first obtained came from the unsymmetrical chloride, while the acid ester is seen to be the final product of the action of alcohols upon both chlorides.

Summary.

1. The paranitroorthosulphone chloride of phenyl benzoate, $C_6H_3(NO_2)\begin{cases}COOC_6H_5\\SO_2Cl\end{cases}$, is formed by the action of phenol on the unsymmetrical chloride, but not from the symmetrical chloride. Ortho- and paracresol act in the same way.

2. The paranitroorthosulphone chloride of ethyl benzoate is formed by the action of ethyl alcohol upon the unsymmetrical chloride, but is not obtained from the symmetrical chloride. Methyl and propyl alcohols act in the same way. By further action of the alcohols, the chlorides are converted into the corresponding acids.

3. The paranitroorthosulphonamide of phenyl benzoate is formed by the action of phenol and ammonia upon the symmetrical chloride, but is not obtained from the unsymmetrical chloride.

4. Both chlorides, when treated with phenol in alkaline solution, give the diesters as the end-products. By modifying the conditions of the experiment, ester chlorides are obtained in the case of phenol and orthocresol.

Contributions from the Chemical Laboratory of the Massachusetts Institute of Technology.

XLII.—THE CONDENSATION OF CARBON TETRACHLORIDE WITH CHLORBENZENE BY MEANS OF THE FRIEDEL AND CRAFTS REACTION.

By James F. Norris and W. C. Twieg.

In a preliminary communication[1] from this laboratory, on the condensation of carbon tetrachloride with certain halogen derivatives of benzene by means of the Friedel and Crafts reaction, it was shown that when chlorbenzene reacts with carbon tetrachloride under these circumstances, but two benzene rings are joined to the methane carbon atom and, as a consequence, a ketone chloride is formed. As with benzene, however, under the same conditions, three halogen atoms are dis-

[1] Norris and Green: This Journal, 26, 492.

placed and a quantitative yield of triphenylchlormethane is formed,[1] it seemed advisable to continue the study of this reaction. It was shown in the first paper that the product of the reaction, when chlorbenzene was used, could be isolated, after the decomposition of the aluminium addition-product, by distillation under reduced pressure. The substance proved to be an oil which had a constant boiling-point. It was decomposed when warmed with dilute alcohol, and, on cooling, 4,4′-dichlorbenzophenone was deposited in pure condition. The oil, on analysis, gave results agreeing with the formula $(ClC_6H_4)_2C.Cl_2$, and was accordingly considered to be 4,4′-dichlorbenzophenone chloride.

When this oil was obtained by distilling the product of the reaction under diminished pressure, there was left a residue which varied in amount in different experiments. In order to isolate the substance contained in this residue in pure condition, if possible, the reaction was more fully studied, with the hope of obtaining trichlortriphenylchlormethane, the substance which would be formed if the reaction proceeded as in the case of benzene and carbon tetrachloride. This compound, as well as the ketone chloride formed, was required for investigations which are now being carried out in this laboratory.

New methods for the isolation of the reaction-products were studied and, as a consequence, it was discovered that the oil previously described as 4,4′-diehlorbenzophenone chloride consisted of a mixture of two isomers. The dipara-compound was present, but mixed with it was a quantity of an isomer, which was shown to have, in all probability, the structure of 2,4′-dichlorbenzophenone chloride.

The ketone chlorides could not be separated, as their boiling-points were very close together, and as they, apparently, formed a constant-boiling mixture. To effect the separation, the chlorides were first converted into the corresponding ketones. The dipara-compound was slightly soluble in cold alcohol and in cold ligroin, while the orthopara-compound was readily soluble in both solvents.

[1] This JOURNAL, 28, 54.

A substance which was identical with the isomer of the dipara-ketone was prepared by the condensation of orthochlorbenzoyl chloride with chlorbenzene. It has been shown that when benzoyl chloride is condensed with chlorbenzene, the benzoyl group takes the position para to the halogen atom in the benzene ring. It follows, therefore, that the isomer has, in all probability, the orthopara-structure. In the first paper on this subject, the fact was mentioned that a small quantity of a compound was obtained which melted at 66° to 68°. This substance we have now shown to be the isomer of 4,4′-dichlorbenzophenone.

As it was found impossible to separate the original products of the reaction between carbon tetrachloride and chlorbenzene, the crude reaction-product, after decomposition with water to remove the aluminium chloride, was treated with concentrated sulphuric acid, in which it was slowly soluble with evolution of hydrogen chloride. When the acid was no longer given off, the product was poured into water. In this way the halogen atoms attached to the methane carbon atom were replaced by oxygen. The mixture so obtained could now be separated into its constituents. By treatment with ligroin, everything but the dipara-ketone was dissolved. By distilling the soluble portion under reduced pressure, the ortho-para-ketone was separated from a residue which could not be distilled. When a solution of the mixture in alcohol, after the removal of the dipara-ketone, was allowed to evaporate slowly, a mixture of the crystals of the orthoparadichlorketone and an oil was obtained. From the reactions, properties, and method of preparation of this oil, it was probably a third possible isomeric ketone—2,2′-dichlorbenzophenone. It could not be obtained in pure condition, as it decomposed when heated under a pressure of 18 mm. Trichlortriphenylchlormethane may have been formed in the reaction, but its presence was not discovered.

It is probable, therefore, that when carbon tetrachloride is condensed with chlorbenzene by the Friedel and Crafts reaction, but two chlorine atoms of the tetrachloride are displaced and that three dichlorbenzophenone chlorides are thus formed.

This result is of interest in connection with the results obtained with benzene where, under the same conditions, three chlorine atoms are removed and triphenylchlormethane is formed.

In one experiment a separation of the reaction-products was made as accurately as possible. From 60 grams of carbon tetrachloride there were obtained 25 grams of the diparaketone, 27 grams of the orthopara-compound, and 36 grams of the oil. In another experiment the mixture of the dipara- and orthoparadichlorbenzophenone chlorides, which distilled at a constant boiling-point, was converted into the corresponding ketones. Eighteen grams of the dipara- and 13 grams of the orthopara- compounds were obtained.

In view of the work which has been done on the condensation of chlorbenzene in the Friedel and Crafts reaction, the results are of interest, inasmuch as in the past it has been found that the para position is the one taken by the entering group almost to the exclusion of the ortho position.

The work on the condensation of paradichlorbenzene with carbon tetrachloride has been continued, as the ketone chloride produced is being used in another investigation. The method of carrying out the reaction has been so improved that the yield of 2,5,2′,5′-tetrachlorbenzophenone chloride has been increased to nearly four times that previously obtained.

EXPERIMENTAL.

A condensation of carbon tetrachloride was carried out as described in the paper referred to above, using 60 grams of carbon tetrachloride (1 molecule), 84 grams of chlorbenzene (2 molecules), 90 grams of aluminium chloride (1.75 molecules), and 300 cc. carbon bisulphide. Sixty grams of an oil boiling at 232° to 233°, at 25 mm. pressure, were obtained. This oil proved to be a mixture of the chlorides of 4,4′- and 2,4′-dichlorbenzophenones. The non-volatile residue weighed 15 grams. By increasing the amount of aluminium chloride to 120 grams, the yield was increased to 80 grams.

A portion of this distillate was decomposed by shaking with concentrated sulphuric acid. When all had passed into solu-

tion, the mixture was poured into water. The resulting ketones, after drying, were separated by warming them with ligroin. On cooling, nearly all the 4,4′-dichlorbenzophenone crystallized out. The soluble part was purified by repeated crystallization from dilute alcohol. Forty grams of the mixed chlorides gave 18 grams of the pure 4,4′-dichlorbenzophenone and 13 grams of the 2,4′-dichlorbenzophenone.

In another experiment the procedure was changed to that most favorable to the formation of a compound containing three benzene rings. Sixty grams of carbon tetrachloride (1 molecule), 120 grams of powdered aluminium chloride, and 126 grams of chlorbenzene (3 molecules) were allowed to react in the presence of 300 cc. of carbon bisulphide. After the mixture had stood over night, during which time a large quantity of hydrogen chloride was evolved, it was heated on a water-bath for a number of hours. After decomposition of the reaction-product by water, the organic part was extracted with carbon bisulphide, which was then removed by distillation. The residue was allowed to stand with concentrated sulphuric acid. When hydrogen chloride was no longer given off, the mixture was extracted with carbon bisulphide in order to remove the excess of chlorbenzene. As but 10 grams of an oil insoluble in sulphuric acid were obtained, and as only one-half of this proved to be chlorbenzene, it seems probable that more than 2 molecules of chlorbenzene had entered into reaction. No evidence of this, however, was obtained by a study of the reaction-product. The solution in sulphuric acid was poured into water. After the separation of the mixture from the dilute acid the former was treated with warm ligroin until the residue became crystalline. After standing some time, 22 grams of 4,4′-dichlorbenzophenone were left undissolved. This was purified by recrystallization from warm alcohol. The ligroin was separated from the part which had dissolved. An attempt was made to separate a small part of the residue into its constituents by crystallization. As a mixture of an oil and ill-defined crystals was obtained, the major part of the product was subjected to distillation at 23 mm. Under these circumstances, the 2,4′-dichlor-

benzophenone distilled unchanged. On recrystallization, the distillate was found to contain a small amount of the dipara-compound. As a result of the experiment, 24 grams of 4,4'-dichlorbenzophenone and 27 grams of 2,4'-dichlorbenzophenone were obtained. The large residue could not be distilled or brought to crystallization.

Preparation of 2,4'-Dichlorbenzophenone from o-Chlorbenzoic Acid.—Ten grams of *o*-chlorbenzoic acid and 13 grams of phosphorus pentachloride were heated under a return condenser on a water-bath for several hours. On distillation, 6.5 grams of the acid chloride, boiling at 228°, were obtained. The product was dissolved in 100 cc. of carbon bisulphide, to which were added 4.5 grams of chlorbenzene and 5 grams of aluminium chloride. After standing a few hours, the mixture was heated on a water-bath for a short time. After the decomposition of the aluminium compound, the product was taken up in carbon bisulphide and treated with dilute alkali. One gram of *o*-chlorbenzoic acid was recovered. After removal of the solvent, the residue was taken up in alcohol. Upon slow evaporation, stout, white needles, which melted at 66° to 68°, separated. Finally a mixture of white needles and a red oil was left. The oil was removed from the crystals by filtration when the solvent had evaporated. The oil appeared to resemble the undistillable part of the reaction-product described above. The yield of the crystals was 4.35 grams. These proved to be identical with the low-melting ketone obtained from carbon tetrachloride. When recrystallized from alcohol, the pure compound was obtained as stout, colorless prisms, which melted at 66°.5 to 67°. A portion of this ketone obtained from the Friedel and Crafts reaction was found to boil at 214° to 215° at 22 mm. A determination of chlorine in the ketone gave 28.28 and 28.41 per cent, while the theory required 28.28 per cent. The compound is soluble in most organic solvents. It crystallizes best from ligroin or cold, dilute 60 to 75 per cent alcohol.

2,4'-Dichlorbenzophenone Chloride.—Seventeen grams of the ketone and 14 grams of phosphorus pentachloride were heated on the water-bath for a few hours. The mixture was then

distilled under diminished pressure. The chloride distilled as a colorless, syrupy oil at 236°, at 34 mm. When redistilled, it boiled at 223° at 23 mm. The oil did not solidify in a freezing-mixture. It was soluble in most organic solvents and was readily converted into the corresponding ketone.

4,4′-Dichlorbenzophenone Chloride.—Twenty-seven grams of pure 4,4′-dichlorbenzophenone (the boiling-point of which was found to be 243° at 38 mm.) was heated with 23 grams of phosphorus pentachloride on an oil-bath, at 150° for one hour. On distillation, 28 grams of product were obtained. When treated with ligroin, in which the chloride is soluble, it was found that 5 grams of the ketone had distilled unchanged. Accordingly, a higher temperature was used in the next experiment.

Forty-four grams of the ketone were heated with 38 grams of phosphorus pentachloride at 170° to 180° for four hours. When distilled, 24.5 grams of the ketone chloride were obtained. A high-boiling residue was left. The action of the phosphorus pentachloride was evidently carried too far. When redistilled, the chloride boiled at 223° at 18 mm. The oily distillate soon changed to a mass of stout, prismatic crystals, which melted at 52° to 53°. The ketone chloride is readily soluble in ligroin, from which it crystallizes readily. When treated with dilute alcohol or with concentrated sulphuric acid, it is converted into 4,4′-dichlorbenzophenone.

2,5,2′,5′-Tetrachlorbenzophenone Chloride.—A study of the best conditions for the condensation of carbon tetrachloride with *p*-dichlorbenzene led to the following results: Ten grams of carbon tetrachloride, 20 grams of *p*-dichlorbenzene, 50 cc. of carbon bisulphide, and 20 grams of *powdered* aluminium chloride were heated on a steam-bath for three hours. The insoluble aluminium compound was washed with carbon bisulphide and then decomposed by water. The organic product was extracted with carbon bisulphide and the solution so obtained evaporated to a small bulk. On slow evaporation, the chloride of 2,5,2′,5′-tetrachlorbenzophenone was deposited in large, brilliant, colorless crystals. By treatment with a small quantity of ether the coloring-matter was re-

moved. When the above proportions were used, 18 grams of the pure compound were obtained. The analysis and properties of the compound were given in the former paper.

BOSTON, MASS., July 10, 1903.

Preliminary Report from the Kent Chemical Laboratory of the University of Chicago.

THE "BECKMANN REARRANGEMENT." III.

STEREOISOMERIC CHLORIMIDO ACID ETHERS.

BY JULIUS STIEGLITZ AND RICHARD B. EARLE.

In two previous papers[1] on the "Beckmann rearrangement," one of us called attention to the importance of determining the rôle of the hydrogen atom, H*, when the acylhalogenamides, RCONH*Hal, are made to suffer a "Beckmann rearrangement" to amines and their derivatives (Hofmann's reaction) under the influence of alkalies. It was shown by Stieglitz and Slosson that no such rearrangement could be effected after the hydrogen atom was replaced by an alkyl or alphyl group with the production of the two possible isomeric series, the acylalkylhalogenamines, RCO(NR'Hal), and the halogenimidoesters, RC(OR')(NHal). The alkyl derivatives are comparatively stable compounds, a fact which is especially impressive in the case of the more interesting of the two series, the halogenimidoesters. They have the same constitution as the metal salts,[2] RC(OMe)(NHal), of the parent substance, salts which, as is well known, suffer the rearrangement with remarkable ease at rather low temperatures (0° to 30°). But methyl chlorimidometanitrobenzoate, for instance, may be heated to 140° without undergoing any change.

This remarkable stability of the ethers, which have the same constitution as the salts, seemed altogether incompatible[3] with the most generally accepted explanation of the "Beckmann rearrangement," that of Hoogewerff and van Dorp,[4] as a di-

[1] Stieglitz: This JOURNAL, 18, 751 (1896); 29, 49 (1903); and also the investigations with E. E. Slosson: Ber. d. chem. Ges., 28, 3266 (1895); 34, 1613 (1901); This JOURNAL, 29, 289 (1903).

[2] Hantzsch: Ber. d. chem. Ges., 35, 228 (1902); Stieglitz and Ransom: *Ibid.*, 34, 1615 (1901) (footnote); This JOURNAL, 29, 64 (1903).

[3] Stieglitz: This JOURNAL, 29, 49 (1903).

[4] Rec. trav. chim. Pays-Bas., 6, 373 (1887), etc.

rect exchange of an alkyl group for a halogen atom caused by the greater affinity of nitrogen for carbon radicals than for halogens. On the basis of the newly proved constitution of the salts of the acylhalogenamides, Hantzsch[1] recently formulated the conception of Hoogewerff and van Dorp as follows:

$$\begin{array}{c} RCOMe \\ \| \\ BrN \end{array} \longrightarrow \begin{array}{c} BrCOMe \\ \| \\ RN \end{array}$$

The alkali used in the reaction is supposed to be necessary only in order to produce the double bond between the carbon and the nitrogen atoms and thus to bring the alkyl group and the bromine atom into favorable proximity for an exchange of positions.

Our only hesitation in rejecting this interpretation absolutely on the basis of the proved stability of the corresponding alkyl ethers arose from the fact that these chlorimidoethers had been obtained by us only in one form, and it was still possible[2] that this one known form might belong to a stable *anti*-series, the rearranging salts to a *syn*-series of stereoisomers, as expressed in the following formulas:

$$\begin{array}{c} RCOR' \\ \| \\ NCl \\ \text{"}\textit{Anti}\text{."} \end{array} \qquad \text{and} \qquad \begin{array}{c} RCOMe \\ \| \\ ClN \\ \text{"}\textit{Syn}\text{."} \end{array}$$

We have, therefore, continued our efforts to prepare stereoisomeric ethers in order to test experimentally this last possible objection to our argument against Hoogewerff and van Dorp's interpretation of the "Beckmann rearrangement." We believe that we have at length succeeded in isolating a pair of such stereoisomers, *viz.*, two methyl ethers of chlorimidometanitrobenzoic acid. These bodies represent, at the same time, the simplest case of *cis-trans* isomerism of nitrogen compounds as yet discovered. As is well known, such a form of stereoisomerism has hitherto been observed with any certainty only in the case of oximes, hydrazones, and some diazo compounds. In all of these cases the third bond of the

[1] Ber. d. chem. Ges., **35**, 3579 (1902).

[2] Stieglitz: This JOURNAL, **18**, 751 (1896); **29**, 55 (1903).

doubly bound nitrogen atom carries some radical, *e. g.*, OH, NHC_6H_5; in no case, however, a single atom like that of chlorine, although, for theoretical reasons, earnest efforts have often been made to prepare such simple representatives of the type of stereoisomerism elaborated by Hantzsch and Werner. The new isomers form this long-missed link in their fruitful theory.

The isomers were discovered only a few weeks ago. But as our work is about to be interrupted for half a year, we feel obliged to publish our results at once in order to hold the field of work.[1] We have already been able to prove that the two ethers in question are identical as regards constitution and molecular weight, and we also have excluded experimentally the possibility of physical isomerism (crystal modifications). All possible forms of isomerism, excepting that of stereoisomerism, having thus been excluded, the two ethers must be space isomers. On the basis of the theory of Hantzsch and Werner, the relation would be that of *syn*- and *anti*-forms, *viz.*:

$NO_2C_6H_4C.OCH_3$ ‖ ClN — "*Syn.*"

$NO_2C_6H_4C.OCH_3$ ‖ NCl — "*Anti.*"

Although time and material were lacking for a complete examination of the chemical changes of the isomers, we have been able to show that both isomers are stable bodies which remain unchanged when warmed for some time to 80°, or even when heated a few minutes to 140°. Consequently, neither suffers a "Beckmann rearrangement" under the influence of heat. We have never observed, as yet, a change of one stereoisomer into the other. The absence of the tendency to rearrangement in both cases is not at all due then to any possible tendency of a reactive *syn*-form to go over into a more stable *anti*-form under the conditions which are used to rearrange the metal salts. Our observations up to the present, therefore, strengthen most decidedly our objections

[1] In the autumn the preparation of other stereoisomeric nitrogen halides will be attempted (the salts of the acylhalogenamides also exist possibly in two forms). The parent substances of the chlorimido ethers, the imido ethers, and their derivatives will also be examined in this direction.

to the interpretation of the "Beckmann rearrangement" given by Hoogewerff and van Dorp and by Hantzsch, and favor the explanation of the reaction given by one of us.[1]

EXPERIMENTAL PART.

In the attempts to prepare stereoisomeric chlorimidoesters, we were guided by the idea that an acylchloramide which forms with alkalies rearranging salts, possibly of a *syn*-series, might give by methylation with diazomethane[2] an ether of the same reactive series, different from the chlorimidoether obtained in the usual way by the action of hypochlorous acid on an imidoether.[3] At the same time it was desirable to obtain any stereoisomers in a solid form, and for that reason derivatives of metanitrobenzoic acid were first employed. We found that the action of hypochlorous acid on methylimidometanitrobenzoate resulted in the formation of both stereoisomers at the same time. They were separated from each other by repeated recrystallization. The action of diazomethane on nitrobenzchloramide gave a much less pure product, from which only the higher-melting isomer, which we will call the α-body for the present, was obtained in a pure condition.

m-Nitrobenzchloramide, *m*-$NO_2C_6H_4CONHCl$, was prepared according to the method of Graebe and Rostovzeff[4] from nitrobenzamide and sodium hypochlorite. Acetic acid precipitated the chloramide as a colorless, gelatinous mass. When dry, it was recrystallized from a mixture of acetone and benzene. It melts at 183° to 184° with decomposition. A quantitative yield was obtained.

For analysis, as in the case of all the nitrogen halides described in this paper, the compound was dissolved in alcohol and treated with a solution of potassium iodide acidified with acetic acid. The iodine which was liberated was titrated against standard thiosulphate solution.

I. 0.1114 gram substance gave 0.0196 gram Cl.
II. 0.1699 gram substance gave 0.0302 gram Cl.

[1] Stieglitz: This JOURNAL, *loc. cit.*
[2] Stieglitz and Ransom: *Ibid.*, **29**, 49 (1903).
[3] Stieglitz: *Ibid.*, **18**, 751 (1896).
[4] Ber. d. chem. Ges., **35**, 2750 (1902).

	Calculated for $C_7H_5O_3N_2Cl$.	Found. I.	II.
Cl	17.67	17.55	17.77

Action of Diazomethane on m-Nitrobenzchloramide.

Methyl Chlorimido-m-nitrobenzoate (*α-body*), $NO_2C_6H_4C(:NCl)OCH_3$.—The chloramide is suspended in anhydrous ether and diazomethane passed into the mixture until the solution appears distinctly yellow. The action takes place tolerably fast at ordinary temperatures and may be hastened by warming the mixture on the water-bath. It is complete as soon as all the solid substance has dissolved. On evaporation of the ether in a vacuum, long, prismatic crystals of the chlorimidoether are deposited. It is purified by repeated precipitation from its solution in chloroform by means of low-boiling ligroin.

I. 0.1532 gram substance gave 0.0250 gram Cl.
II. 0.1365 gram substance gave 0.0222 gram Cl.

	Calculated for $C_8H_7O_3N_2Cl$.	Found. I.	II.
Cl	16.52	16.33	16.29

The compound crystallizes from chloroform and ligroin in fan-like groups of silky needles. By the slow evaporation of the solutions, long prisms or rectangular plates are obtained (see Fig. I.). The substance melts at 86°.5 to 87°.5 without decomposition, and melts at the same point if it is allowed to

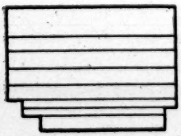


Fig. 1. α-body.

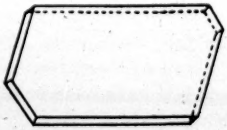


Fig. 2. β-body.

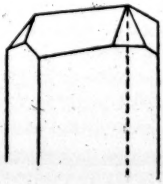


Fig. 3.

solidify and is heated once more. It is easily soluble in chloroform, benzene, and acetone; quite soluble in ether and warm ligroin, hardly soluble in cold ligroin. A more de-

tailed description of the physical properties of the compound will be given below, when it will be compared with the stereoisomer, which will be called for the present the *β*-body.

The constitution of the *α*-body was determined by treatment of the substance with dry hydrogen chloride in the presence of ligroin. The hydrochloride of methyl imido-*m*-nitrobenzoate was obtained according to:[1]

$$NO_2C_6H_4C(:NCl)OCH_3 + 2HCl \rightarrow NO_2C_6H_4C(:NH)OCH_3,HCl + Cl_2.$$

The hydrochloride of the imidoether decomposed, when melted, into methyl chloride and *m*-nitrobenzamide:

$$NO_2C_6H_4C(NH)OCH_3,HCl \rightarrow CH_3Cl + NO_2C_6H_4CONH_2.$$

The amide was identified by its melting-point, which was not depressed by the admixture of some synthetic *m*-nitrobenzamide (m. p. 142°).

The hydrochloride of methyl imido-*m*-nitrobenzoate obtained from the *α*-body was also identified by the fact that with cold water it gave ammonium chloride and methyl *m*-nitrobenzoate (m. p. 75° to 76°):

$$NO_2C_6H_4C(NH)OCH_3,HCl + H_2O \rightarrow NO_2C_6H_4CO_2CH_3 + NH_4Cl.$$

In a roughly quantitative study of the action of dry hydrogen chloride on the *α*-body, 0.163 gram substance gave 0.151 gram of the hydrochloride of the imidoether, or 91.8 per cent of the theoretical yield. From the salt, 0.109 gram methyl *m*-nitrobenzoate was obtained by the action of water, that is 86.5 per cent of the calculated yield. The fact thus established, that in the *α*-body the methyl group is attached to the oxygen atom of the acid radical, is confirmed by the proof brought below, that the only possible constitutional isomer, *m*-nitrobenzmethylchloramine, $NO_2C_6H_4CO(NClCH_3)$, is an entirely different substance.

The action of diazomethane on *m*-nitrobenzchloramine takes place, therefore, according to:

[1] Stieglitz: This JOURNAL, 18, 751 (1896).

$$NO_2C_6H_4CONHCl + CH_3N_2 \rightarrow NO_2C_6H_4C(OCH_3)(:NCl) + N_2,$$

and the constitution of the α-body is that given in this equation.

The Action of Hypochlorous Acid on Methyl Imido-m-nitrobenzoate.

The hydrochloride of methyl imido-*m*-nitrobenzoate (15 grams) is added rapidly to a large excess of sodium hypochlorite[1] at 30°.[2] An oil separates instantly and then solidifies in a few moments. The crude product is washed with cold water and then dried on clay plates. The average yield is 9 to 10 grams. The crude product melts at 63° to 68°. After two recrystallizations from ligroin the α-modification of methyl chlorimido-*m*-nitrobenzoate is first precipitated, together with small quantities of the β-body, which lowers the melting-point from 87° to 79°. That the substance is otherwise pure is shown by the following analysis:

0.1891 gram substance gave 0.0315 gram Cl.

	Calculated for $C_8H_7O_4N_2Cl$.	Found.
Cl	16.52	16.64

From the mother-liquors, crystals are obtained which melt at 56° to 63°, and the analyses of which also prove them to be pure methyl chlorimido-*m*-nitrobenzoate, but these crystals consist of mixtures of the two stereoisomeric bodies (the α- and the β-modifications). The analyses of several of these low-melting mixtures are given in order to show that we have to do from the beginning with mixtures of the pure isomers:

I. 0.1660 gram substance gave 0.0273 gram Cl.
II. 0.2021 gram substance gave 0.0336 gram Cl.
III. 0.1468 gram substance gave 0.0244 gram Cl.

	Calculated for $C_8H_7O_4N_2Cl$.	Found. I.	II.	III.
Cl	16.52	16.44	16.63	16.63

From this mixture the two isomers were isolated in a pure condition by repeated recrystallization. We found the best

[1] Prepared according to Graebe's method (*loc. cit.*).
[2] At 0° the reaction-products and the yields are the same.

procedure to be the following: The crude product is extracted three times with some boiling ligroin (b. p. 40°) and the residue is dissolved in chloroform and an excess of ligroin added to the solution. The α-body is precipitated in a fairly pure condition (m. p. 79°). By repeated recrystallization from chloroform and ligroin, it is obtained absolutely free from the β-body, and melts then at 87°.5. This melting-point is the same as that of the compound obtained from nitrobenzchloramide and diazomethane. A mixture of crystals of the compound prepared by the two methods of formation also melted at 87°.5. The formation of methyl chlorimido-*m*-nitrobenzoate (α-body) from methyl imido-*m*-nitrobenzoate and hypochlorous acid is expressed by the equation:

$$NO_2C_6H_4C(:NH)OCH_3 + HOCl \rightarrow NO_2C_6H_4C(:NCl)OCH_3 + H_2O.$$

Methyl Chlorimido-m-nitrobenzoate (β-*body*), $NO_2C_6H_4C(:NCl)OCH_3$. — The second stereoisomer, the β-body, is obtained from the first extracts of the crude material with boiling ligroin and from the mother-liquors obtained in the isolation of the α-body. After the evaporation of the solvents, the residue which still contains considerable quantities of the α-body, is dissolved once more in chloroform, ligroin added to the solution, and, after a short time, the supernatant liquid poured off from the precipitated crystals of the α-body, and allowed to evaporate spontaneously. Needle-shaped crystals of the less soluble α-modification, mixed with some of the β-form, are deposited on the sides of the vessel, and larger, rhombic crystals of the β-body are deposited on the bottom of the vessel. The latter are now almost pure and melt at 79°. The addition of some of the α-body depresses the melting-point to 63° to 70°. One or two further recrystallizations by the method of evaporation, as just described, raise the melting-point of the β-modification to 81°–82°, and further recrystallizations then leave the melting-point unchanged. The yield of the pure β-body was rather small, no doubt partly in consequence of the very long method of purification that had to be used. Several grams,

however, were obtained in the course of our working up some 100 grams of crude material in several portions.

I. 0.1133 gram substance gave 0.0189 gram Cl.
II. 0.1601 gram substance gave 0.0264 gram Cl.

	Calculated for $C_8H_7O_3N_2Cl$.	Found. I.	II.
Cl	16.52	16.68	16.50

The β-body has the same constitution as the α-body. The possibility of its having been formed by a molecular rearrangement[1] according to

$$NO_2C_6H_4C(OCH_3)(NCl) \rightarrow NO_2C_6H_4CO(NClCH_3),$$

was excluded by the preparation of *m*-nitrobenzoylmethylchloramine (see below) as well as by the action of dry hydrogen chloride on the β-body in the presence of ligroin. In the latter experiment, exactly the same result was obtained as in the case of the α-body. The hydrochloride of methyl imidonitrobenzoate was formed. It melted at 127° with evolution of methyl chloride and formation of *m*-nitrobenzamide. The latter was recrystallized once from hot water and melted at 140°. Mixed with some synthetically prepared *m*-nitrobenzamide (m. p. 142°), it melted at 141°. The hydrochloride of the imidoether also gave, with water, methyl *m*-nitrobenzoate (m. p. 77°). In a roughly quantitative experiment we obtained from 0.179 gram of the purest β-compound 0.160 gram of the hydrochloride of the imidoether, or 94 per cent of the calculated amount. From the salt, 0.118 gram of methyl *m*-nitrobenzoate (m. p. 76° to 77°) was obtained by the action of water, that is 88 per cent of the calculated amount. A mixture was prepared of the methyl *m*-nitrobenzoate (m. p. 76° to 77°) obtained from the β-body and the methyl *m*-nitrobenzoate (m. p. 76° to 77°) obtained from the α-body (see above). The mixture also melted at 76° to 77°. There is no doubt, therefore, that in both the α- and β-bodies the methyl group is attached to the oxygen atom of the acid radical, and the nitro group is in the same position (meta) relative to the

[1] Imidoethers suffer such a rearrangement when they are heated with methyl odide, but not under the conditions used above.

acid radical—in a word, that the two bodies have the same constitution and are methyl chlorimido-*m*-nitrobenzoates.

N-Methyl-m-nitrobenzchloramide, $NO_2C_6H_4CO(NClCH_3)$, was prepared in order to exclude the possibility that we had mistaken it for one of the described modifications of the isomeric oxygen ether of the chloramide. Two grams of *m*-nitrobenzmethylamide (m. p. 176°), prepared from *m*-nitrobenzoylchloride and methylamine, was suspended in 100 cc. of water at 40°, and the chlorine evolved by the action of 8 grams of potassium permanganate on hydrochloric acid was passed into the mixture. The crystals were converted into a more flocculent precipitate. The compound was washed with water and then dried and recrystallized once from ligroin (b. p. 70° to 80°).

0.2143 gram substance gave 0.0356 gram Cl.

	Calculated for $C_8H_7O_3N_2Cl$.	Found.
Cl	16.52	16.62

The melting-point of this nitrogen ether was found to be 76° to 77°, which is rather close to the melting-points of the isomeric oxygen ethers. But we found in repeated experiments that mixtures of equal quantities of the nitrogen ether (m. p. 77°), and either the α-body (m. p. 87°) or the β-body (m. p. 81°) invariably melted much lower than any of the compounds, *viz.*, at 60° to 68°. There can be no doubt, therefore, that the nitrogen ether is entirely distinct from either of the two other isomers. It crystallizes in thick, monoclinic prisms with characteristic ends (see Fig. III.), quite different from the crystal forms of the two oxygen ethers. Treated with dry hydrogen chloride in the presence of ligroin, it is converted into *m*-nitrobenzmethylamide, a reversal of the method we used in preparing it.

$$NO_2C_6H_4CONHCH_3 + Cl_2 \rightleftharpoons NO_2C_6H_4CONClCH_3 + HCl.$$

Comparison of the α- and β-Modifications of Methyl Chlorimido-m-nitrobenzoate.

The Crystal Forms.—The difference in the crystalline structure of the two stereoisomers is apparent even to the naked

eye. The α-body forms needles which have a soft, silky luster; the β-body crystallizes in granular masses. Under the microscope the α-compound appears in long needles, grouped in clusters. When it is allowed to crystallize slowly, by the evaporation of its solutions at ordinary temperatures, it forms rectangular plates (see Fig. I.). The β-compound appears under the microscope in the form of very thin rhombohedric plates, which grow in separate crystals (see Fig. II.).

The Molecular Weight.—The molecular weights were determined by the cryoscopic method, benzene being used as solvent. In the calculation of the results, 53 was used as the constant for benzene, this being its theoretical value as calculated from the melting-point and the heat of fusion of the solvent. If the empirical constant, 49, is taken, as is often done, the molecular weights found for the α- and β-varieties are about 8 per cent lower than those given below, but they still agree perfectly with each other and satisfactorily with the theoretical molecular weight.

1. The α-body (m. p. 86° to 88°). 21.79 grams solvent.

I. 0.1596 gram substance gave 0°.189 depression.[1]
II. 0.3098 gram substance gave 0°.360 depression.
III. 0.4624 gram substance gave 0°.518 depression.

	Calculated for $C_8H_7O_2N_2Cl$.	Found. I.	II.	III.
Molec. wt.	214.5	204	206	215

2. The β-body (m. p. 77°).[2] 21.03 grams solvent.

I. 0.1444 gram substance gave 0°.184 depression.
II. 0.3054 gram substance gave 0°.375 depression.
III. 0.4788 gram substance gave 0°.569 depression.

	Calculated for $C_8H_7O_2N_2Cl$.	Found. I.	II.	III.
Molec. wt.	214.5	196.5	202.5	207

3. A mixture of the α- and β-bodies (m. p. 67°).[3] 21.89 grams solvent.

I. 0.1468 gram substance gave 0°.168 depression.

[1] The mean of two or three readings is always given.

[2] The melting-point fell to 63° to 65° when a little of the α-body was added to the substance.

[3] Analysis: Calculated, Cl 16.53; found, Cl 16.63.

II. 0.2988 gram substance gave 0°.331 depression.
III. 0.4572 gram substance gave 0°.500 depression.

	Calculated for $C_8H_7O_3N_2Cl$.	Found. I.	II.	III.
Molec. wt.	214.5	210	216	217

The Melting-points.—1. Each isomer, added to the other one, both being absolutely pure, causes a decided depression of the melting-point of the body used. The melting-point of the α-body is depressed from 87° to 63°–65°, that of the β-body from 82° to 63°–65°, when approximately equal quantities of the two isomers are mixed and the depression is roughly in proportion to the amount of the foreign isomer added.

2. Each body, when it is melted and allowed to solidify again, always gives the same melting-point as the original substance used.[1] There is, consequently, no transformation of one isomer into the other when the bodies crystallize from the liquid condition.

3. If the α-body is fused and made to solidify again with the aid of a glass rod, to which a very small quantity of the β-body has been made to adhere, it still remains the α-body in spite of the contact with the β-isomer at the moment of crystallization. In consequence of the admixture of the small quantity of the foreign isomer, its melting-point sinks from 87°.5 to 85°–86° and it is reduced to 63° to 70° by the addition of still more of the β-form.

Exactly the same results are obtained with the β-body when it is allowed to crystallize in contact with very small amounts of the α-body. It always preserves its own identity; the melting-point is never raised but is depressed, roughly, in proportion to the amount of the foreign isomer used. The same observations are also made when the liquid condition is produced by evaporation of a solution rather than by fusion and crystallization allowed to proceed in contact with the foreign isomer.

These results, together with the fact that a transformation

[1] The compounds must be perfectly pure. Otherwise the β-form occasionally shows, after fusion and recrystallization, a depression of 10°, probably in consequence of some decomposition (coloration).

of either of the isomers into the other one has never been observed under any conditions, and that the two isomers crystallize side by side from the same solutions in ligroin, completely exclude, we believe, the possibility that the two forms are physical (crystal) isomers of the same compound.

Physical and structural isomerism thus being excluded and the molecular weights of the two bodies being identical, the latter must be stereoisomers. They are, therefore, no doubt *syn-* and *anti*-isomers, as explained in the introduction (page 400). No other known form of stereoisomerism would obtain for compounds of this constitution. As no reliable basis for distinguishing either form as the *syn-* or *anti*-isomer has yet been found, we will leave the determination of this question to a future investigation.

The Action of Heat on the Stereoisomers.

The action of heat on the two stereoisomers was studied first as being of peculiar interest, because the corresponding sodium salt of *m*-nitrobenzbromamine,

$$NO_2C_6H_4C(:NBr)ONa,$$

suffers a "Beckmann rearrangement" when it is warmed in an aqueous[1] or alcoholic[2] solution. If the alkali metal is only necessary to produce the double bond between carbon and nitrogen in order to effect the rearrangement,[3] then at least one of the stereoisomeric esters should suffer a similar rearrangement when heated or even warmed.

1. 0.0778 gram of the almost pure β-compound (m. p. 77° to 79°) was heated for forty minutes at 80° to 85° in a flask closed by a tube containing calcium chloride. A trace of substance sublimed. The residue (0.0766 gram) was analyzed by means of potassium iodide and thiosulphate and gave 16.78 per cent active chlorine (16.53 per cent is the calculated amount for the unchanged substance). In a second experiment, some of the purest preparation of the β-compound (m. p. 81° to 82°) was heated for one hour to 80° to 85°.

[1] Hoogewerff and van Dorp: Rec. trav. chim., Pays-Bas., **8**, 193 (1888).
[2] Polin: This JOURNAL, **19**, 325 (1897).
[3] Hantzsch: Ber. d. chem. Ges., **35**, 3580 (1902).

After solidifying, it again melted at 81° to 82°, and the addition of some of the α-body depressed the melting-point 16°. Consequently, prolonged heating at 80° produces neither a "Beckmann rearrangement" of the β-body nor a transformation into the α-form.

2. 0.0686 gram of the purest β-body was heated for five minutes at 130° to 140°. The residue gave 16.78 per cent active chlorine (calculated 16.53 per cent). Heating the β-body even to 140°, therefore, does not produce a rearrangement. In two other experiments with the β-body, heating to 140° caused in the one case a slight depression of its melting-point (from 82° to 76°), in the second case no depression at all, and in both cases the admixture of some α-body caused a decided depression of the melting-point. Consequently, there is no transformation of the β-body into the α-compound even at 140°.

3. Analogous experiments were carried out with the α-body. Heating it a half hour at 90° to 95°, or five minutes at 130° to 140°, left the body unchanged. Mixed with purest α-body, the solidified, heated sample showed no change of melting-point, and mixed with some β-compound, its melting-point was decidedly depressed, as usual. The α-body, consequently, suffers neither a "Beckmann rearrangement" nor a transformation into the β-body when heated as high as 140°.

CHICAGO, April, 1903.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

THE "BECKMANN REARRANGEMENT." IV.

BY JULIUS STIEGLITZ AND RICHARD B. EARLE.

PART I.

The Formation of Acylalkylureas in Hofmann's Reaction.

In the preparation of an alkylamine, according to Hofmann's method, from an acid halogenamide or from an acid amide, bromine and alkali, by a "Beckmann rearrangement" of the acidamide,[1] an acylalkylurea is often obtained[2] as a by-prod-

[1] Hoogewerff and van Dorp: Rec. trav. chim. Pays-Bas., 6, 373 (1887); 8, 173 (1889), etc.; Stieglitz: This JOURNAL, 18, 751 (1896); 29, 49 (1903).

[2] Hofmann: Ber. d. chem. Ges., 15, 412 (1882).

uct, and it frequently is the main product if an excess of the acid amide is used. Thus 2 molecules of acetamide treated with 1 molecule of bromine and 2 of alkali give a very good yield of acetylmethylurea,[1] only 1 molecule of the amide suffering the characteristic rearrangement:

$$2CH_3CONH_2 + Br_2 + 2NaOH \rightarrow CH_3CONHCONHCH_3 + 2NaBr + 2H_2O \quad (1).$$

In the higher aliphatic series the urea is the main product,[2] even when no excess of the acid amide is used, if aqueous solutions of an alkali are employed to effect the rearrangement. The yield of amine is, consequently, a very poor one. In alcoholic solutions, specific precautions must be taken if a complete rearrangement of a higher aliphatic acid amide is desired, otherwise the acylalkylurea is again the chief product obtained.[3]

The ready formation of these alkylacylureas has been ascribed[4] to the supposed fact that the alkyl isocyanate[5] which forms the first tangible product of the rearrangement of the acylhalogenamide, combines with any excess of acid amide which may be present. The action is supposed to go according to the following two stages:

$$RCONHHal + KOH \rightarrow CO:NR + KHal + H_2O; \quad (2)$$

$$CO:NR + RCONH_2 \rightarrow RCONHCONHR. \quad (3)$$

But this latter condensation actually takes place readily only at elevated temperatures, and Dr. Elizabeth Jeffreys,[6] working under the direction of the one of us, was able to show that neither phenyl isocyanate nor chlorformanilide can be made to combine with an acid amide in the presence of alcohol, a urethane being invariably produced rather than an acylalkylurea.

[1] Hofmann: Ber. d. chem. Ges., 14, 2725 (1881).

[2] Turpin: *Ibid.*, 21, 2488 (1888).

[3] Jeffreys: This JOURNAL, 22, 14 (1889). See also Swartz: *Ibid.*, 19, 295 (1897); and Folin: *Ibid.*, 19, 325 (1897).

[4] Hofmann: Ber. d. chem. Ges., 15, 410 (1882); Graebe and Rostovzeff: *Ibid.*, 35, 2747 (1902).

[5] Or the halogen formamide, (Hal)CONHR, derived from it, Graebe: *Loc. cit.*; Hoogewerff and van Dorp: *Loc. cit.*

[6] *Loc. cit.*, p. 42.

The present investigation was undertaken with the object of determining the real course of the formation of acylalkylureas in Hofmann's reaction, and especially of ascertaining whether their formation under the conditions described above could mean that isocyanates cannot always be accepted as the first intermediate products of the rearrangement of acid halogenamides.[1]

Having found, with Dr. J. H. Ransom, that acid chloramides are very readily methylated by the action of diazomethane,[2] the one of us suspected that the formation of acylalkylureas in Hofmann's reaction is due to the condensation of a molecule of an isocyanate—formed by the rearrangement of 1 molecule of an acid halogenamide—with a second molecule of the acid halogenamide itself, an acylhalogenalkylurea being formed according to:

$$RCONH(Hal) + KOH \rightarrow RN:CO + KHal + H_2O; \quad (4)$$

$$RCONH(Hal) + RN:CO \rightarrow RCON(Hal)CONHR. \quad (5)$$

The urea, containing a nitrogen halide group, would be readily saponified in an alkaline solution[3] and form a hypochlorite, or hypobromite, and an acylalkylurea:

$$RCON(Hal)CONHR + KOH \rightarrow RCONHCONHR + KOHal. \quad (6)$$

The hypochlorite or hypobromite would then be available to act on a further molecule of acid amide, if such were still present, and thus complete the reaction according to the proportions expressed summarily in equation (1).

We have found that, both in the aliphatic and in the aromatic series, acid chloramides do condense, in fact, very readily and sometimes almost explosively with isocyanates, according to equations (5) and (6). Acylalkylureas are obtained very easily at ordinary temperatures in the presence of alkalies, under conditions, therefore, such as actually exist when Hofmann's reaction is carried out. As determined once more, aliphatic and aromatic acid amides do not respond at all to

[1] Stieglitz: This JOURNAL, *loc. cit.*
[2] *Ibid.*, **29**, 49 (1903).
[3] Slosson: *Ibid.*, **29**, 289 (1903).

the action of isocyanates under these circumstances. The formation of acylalkylureas in Hofmann's reaction is consequently due to the ready condensation of an isocyanate, the primary product of the rearrangement of a molecule of an acid halogenamide, with a second molecule of the latter, and to a subsequent saponification of the condensation-product. The action is, therefore, now also in complete harmony with the conception that an isocyanate may always be considered to be the first product of the "Beckmann rearrangement" of an acid halogenamide.

If the condensation of an aromatic isocyanate with an acid halogenamide is carried out in the absence of alkali under conditions, therefore, which would not lead to the saponification of the acylhalogenalkylurea formed primarily—see equations (5) and (6)—the urea is frequently found to suffer spontaneously an inter- or intramolecular migration of the halogen atom into the aromatic nucleus:

$$RCON(Hal)CONHC_6H_5 \rightarrow RCONHCONHC_6H_4(Hal). \quad (7)$$

This rearrangement is somewhat analogous to the transformation of acylphenylhalogenamines into acylhalogenanilides,[1]

$$RCON(Hal)C_6H_5 \rightarrow RCONHC_6H_4(Hal),$$

but it differs from the latter in the fact that the halogen is not attached to the same nitrogen atom as the phenyl group into which it migrates. As the question of the nature of this change of position was not involved directly in our main problem we have left it for possible future investigation. It presents three interesting possibilities: An intramolecular migration between groups of atoms more widely separated than in all the well-known analogous rearrangements; an intermolecular action in contrast to the intramolecular transformation of the acylphenylhalogenamines;[2] and the most attractive possibility of a sequence of two migrations of the chlorine atom as the radical of hypochlorous acid, first from the

[1] Bender: Ber. d. chem. Ges., 19, 2272 (1886); Stieglitz and Slosson: *Ibid.*, 28, 3266 (1896); Slosson: *Loc. cit.*; Chattaway and Orton: J. Chem. Soc. (London), 77, 134 (1900).

[2] Blanksma: Rec. trav. chim. Pays-Bas., 21, 366 (1902).

one nitrogen atom to the other more positive one—as acyl groups actually are known to migrate[1]—and then from the second nitrogen atom into the phenyl ring of the same aniline group.

EXPERIMENTAL PART.

The Action of p-Chlorphenyl Isocyanate on Benzchloramide.

To 4.6 grams (1 mol.) of benzchloramide[2] were added 3 grams (1 mol.) of *p*-chlorphenyl isocyanate,[3] and a solution of 0.9 gram of sodium hydroxide in 9 cc. water. The reaction disengaged considerable heat, and it was necessary to moderate it by cold water. The mixture was shaken vigorously at intervals for half an hour, then the red precipitate was brought on a filter and thoroughly washed with water, alcohol, and finally, ammonia. The substance was extracted several times with boiling alcohol to insure the removal of traces of impurities. The insoluble residue melted at 227°, and was identified as symmetrical benzoyl-*p*-chlorphenylurea by the determination of the melting-point of a mixture of the substance with some of the urea which was prepared synthetically and melted at 235° to 237°. The mixture melted at 233° to 235°. *p*-Chlorphenyl isocyanate had condensed, therefore, with benzchloramide under the conditions of Hofmann's reaction to form symmetrical benzoyl-*p*-chlorphenylurea according to equations (5) and (6).

Symmetrical Benzoyl-p-chlorphenylurea, $C_6H_5CONHCONHC_6H_4Cl$.—The urea was prepared synthetically in two ways: By the action of *p*-chlorphenyl isocyanate on benzamide at 150°, and by the action of benzoyl chloride on *p*-chlorphenylurea. The latter method gave the purest substance. A mixture of benzoyl chloride and the urea was heated for an hour at 110° to 130°. The product was extracted several times with hot alcohol and the very difficultly soluble residue recrystallized from a large amount of boiling

[1] This JOURNAL, **23**, 1 (1900).

[2] Graebe and Rostovzeff: Ber. d. chem. Ges., **35**, 2750 (1902).

[3] The isocyanate was prepared from *p*-chlorphenylurethane and phosphorus pentachloride, according to Lengfeld and Stieglitz: This JOURNAL, **16**, 70 (1894); Folin: *Ibid.*, **19**, 336 (1897).

alcohol. The compound melted then at 235° to 237° and an analysis, (I.), proved its purity. When equivalent quantities of *p*-chlorphenyl isocyanate and benzamide were heated to 150°, the mixture foamed and then quickly solidified. The product, washed for some time with hot alcohol, was analyzed without further purification (Analysis II.). It formed a mass of white needles and melted at 234° to 236°.

I. 0.3026 gram substance gave 0.1581 gram AgCl.
II. 0.2973 gram substance gave 0.1601 gram AgCl.

	Calculated for $C_{14}H_{11}O_2N_2Cl$.	Found. I.	II.
Cl	12.92	12.92	13.31

The Action of Phenyl Isocyanate on Benzchloramide.

This reaction was studied first in the absence of water and alkali. Phenyl isocyanate[1] (1.2 grams) was dissolved in 5 cc. dry benzene and warmed with dry benzchloramide (2 grams). At 77° all the chloramide had dissolved and the liquid became filled with a crystalline solid. After fifteen minutes, it was brought on a filter, washed with cold alcohol and some ammonia, and then thoroughly with boiling alcohol. The insoluble residue melted at 225°, and when added to synthetic symmetrical benzoyl-*p*-chlorphenylurea, it did not appreciably depress the latter's melting-point. It consisted, therefore, of benzoyl-*p*-chlorphenylurea, and it was formed, evidently, as the result of a condensation of phenyl isocyanate with benzchloramide and a subsequent migration of the chlorine atom into the benzene nucleus (see equations 5 and 7).

The action of phenyl isocyanate on benzchloramide in the presence of alkali was next tried. Benzchloramide (1.6 grams) was dissolved at 0° in a 20 per cent solution (7.5 cc.) of sodium hydroxide and this solution added all at once to the phenyl isocyanate (1.1 grams), the mixture being vigorously shaken. A reaction ensued instantly, the odor of hypochlorous acid (from the hydrolysis of some of the hypochlorite formed in the reaction) was developed, and a reddish precipi-

[1] The phenyl isocyanate was prepared from phenylurethane and phosphorus pentachloride, according to the method of Lengfeld and Stieglitz: *Loc. cit.* See Dains: J. Am. Chem. Soc., 21, 165 (1899).

tate formed. The latter was washed with alcohol and ammonia, and recrystallized from hot alcohol. It then melted at 205°, and when it was mixed with some synthetically prepared symmetrical benzoylphenylurea (m. p. 205°) its melting-point remained unchanged. The condensation had, consequently, taken place as expected, according to the equations (5) and (6). It may be added that the reaction does not take place smoothly unless there is at least one equivalent of alkali present as required by these equations.

Phenyl isocyanate also condenses readily with benzbromamide under these same conditions, symmetrical benzoylphenylurea being again formed as the product of the action.

Phenyl Isocyanate and Benzamide.

Benzamide is much less reactive towards phenyl isocyanate than are its chlorine and bromine derivatives, and it does not condense at all with the isocyanate under the conditions of Hofmann's reaction. On warming a solution of the two substances as high as 100°, we found that no reaction had ensued and the benzamide was recovered unchanged. When benzamide was shaken with phenyl isocyanate (1 mol.) and an equivalent amount of sodium hydroxide, in aqueous solution, at ordinary temperatures until no odor of phenyl isocyanate remained discernible, the main reaction-product was aniline, and the benzamide was recovered unchanged. The aniline, obviously, was produced by the action of the alkali on the isocyanate.

The Action of Phenyl Isocyanate on Acetchloramide.

Symmetrical Acetylphenylurea, $CH_3CONHCONHC_6H_5$.—To one equivalent of sodium hydroxide (a 10 per cent solution) 1 molecule of acetchloramide was added and the solution poured at once on an equivalent weight of phenyl isocyanate. The solid, which quickly separated, was collected on a filter, washed with some alcohol and ammonia, and recrystallized from hot water. It melted at 183° to 184°, and a mixture of it and some pure symmetrical acetylphenylurea (m. p. 183° to 184°) gave the same melting-point. The action had proceeded, therefore, as expected, according to

$$CH_3CONHCl + C_6H_5NCO + NaOH \rightarrowtail CH_3CONHCONHC_6H_5 + NaOCl.$$

Acetamide is not acted upon by phenyl isocyanate, when the two are brought together in the presence of an equivalent amount of a five per cent solution of sodium hydroxide. The acetamide may be recovered, together with carbanilide and aniline, decomposition-products of the isocyanate.

The Action of Methyl Isocyanate on Acetchloramide.

Symmetrical Acetylmethylurea, $CH_3CONHCONHCH_3$. — Acetchloramide (1.8 grams) was dissolved in 5.5 cc. of a 20 per cent solution of caustic potash at 0°, and the solution added rapidly to 1.1 grams methyl isocyanate. A violent reaction occurred instantly and completed itself in less than a minute. A white solid filled the liquid. A little ammonia was added to the mixture, the solid collected on a filter, and washed with some cold water. It was fully identified in the usual way as symmetrical acetylmethylurea, by its melting-point (178°.5), and by the fact that this melting-point was not depressed by the addition of some synthetic acetylmethylurea to the reaction-product.

Methyl isocyanate does not combine with acetamide under the same conditions under which it reacts so vigorously with acetchloramide. Not a trace of acetylmethylurea could be obtained, the isocyanate being decomposed into methylamine and carbonic acid.

PART II.

Diacylchloramines.

When benzoylphenylchloramine is decomposed by heat, a little benzoyl chloride is formed,[1] possibly according to the following reaction :[2]

$$C_6H_5CONClC_6H_5 \rightarrowtail C_6H_5COCl + C_6H_5N : . \qquad (1)$$

It was hoped that diacylchloramines might decompose more readily in an analogous fashion, *viz.*, according to

[1] Chattaway and Orton : J. Chem. Soc. (London), 79, 462 (1901) ; Slosson : This JOURNAL, 29, 305 (1903).

[2] The nature of the nitrogenous decomposition-product has never been determined. See Stieglitz : This JOURNAL, 29, 49 (1903).

$$(C_6H_5CO)_2NCl \rightarrow C_6H_5COCl + C_6H_5CON: . \quad (2)$$

An acylimide, with a univalent nitrogen atom, might thus result, which would be identical with the hypothetical substance that is supposed by the one of us to be an important intermediate product in the "Beckmann rearrangement" of acylchloramides, acylazides, oximes, etc.[1] A study of dibenzoylchloramine was, therefore, undertaken in order to ascertain whether it would suffer a "Beckmann rearrangement" under the influence of heat. The experiments showed that the decomposition takes a different course, benzonitrile, chlorine, and benzoyl chloride being the main products. This would indicate that a breaking down into benzonitrile and benzoyl hypochlorite[2] is the primary change:

$$(C_6H_5CO)_2NCl \rightarrow C_6H_5CN + C_6H_5COCl.$$

This decomposition is entirely analogous to that which the parent substance, dibenzamide, undergoes when it is heated:[3]

$$(C_6H_5CO)_2NH \rightarrow C_6H_5CN + C_6H_5COOH.$$

In order to determine whether a small part of the dibenzoylchloramine had suffered a "Beckmann rearrangement," the decomposition-products were completely saponified and tested for aniline, but only doubtful traces of the latter could be detected. This showed that none of the substance had undergone the rearrangement. When dibenzoylchloramine was heated with freshly ignited calcium oxide, the result was the same.

Dibenzoylchlorimide, $(C_6H_5CO)_2NCl$.—The diacylchlorimides were found so sensitive to water, which hydrolyzes them to hypochlorous acid and diacylimides, that it was found necessary to exclude water entirely in order to prepare dibenzoylchlorimide in a pure condition. Two grams of the silver salt of dibenzoylimide, dried at 100°, were suspended in 15 cc. anhydrous chloroform and 0.44 gram carefully dried chlorine passed into the mixture. After filtration the chloroform was

[1] Stieglitz: This JOURNAL, *loc. cit.*, and **18**, 751 (1896).
[2] See Schützenberger's chlorine acetate: Ann. Chem. (Liebig), **120**, 113 (1861).
[3] Krafft: Ber. d. chem. Ges., **23**, 2391 (1890).

evaporated *in vacuo* in a desiccator and the residue recrystallized from ligroin (b. p. 70° to 80°).

I. 0.1379 gram substance gave 0.0184 gram active Cl.

II. 0.1547 gram substance gave 0.0206 gram active Cl.

	Calculated for $C_{14}H_{10}O_2NCl$.	Found. I.	Found. II.
Cl	13.65	13.37	13.32

Dibenzoylchlorimide crystallizes in white needles, which melt at 86°.

Three grams of the chlorimide were heated in a distilling-flask connected with a condenser, in a metal-bath. Decomposition set in at 240° to 260°, and proceeded smoothly, the substance turning dark red. The temperature was kept at 250° to 260° for five minutes. Ammonia was added to the cooled contents of the flask. Benzonitrile, benzoic acid, and benzamide were the only products that could be identified, besides some chlorine which escaped during the decomposition of the substance. In a second experiment, the reaction-product was saponified by being boiled with sulphuric acid (sp. gr. 1.44), and the mixture tested for aniline as follows: It was made alkaline, distilled with steam, and the distillate tested directly for traces of aniline, as well as extracted with ether, the test for aniline being made after the evaporation of the extract in the cold. No trace of aniline could be found. Preliminary tests showed that a few milligrams of carbanilide or phenylurea, subjected to this treatment, easily give the aniline reactions.

An intimate mixture of 1.5 grams dibenzoylchloramine and 0.2 gram freshly ignited calcium oxide was heated to 170° to 180°. Benzonitrile and its polymer, cyanphenine, were the only nitrogenous products obtained in quantity. Tests for aniline were made as in the previous experiment. Once a trace of it was shown by the chloride of lime test, but in a duplicate experiment not even this trace was found.

It is evident, therefore, that dibenzoylchlorimide does not show any tendency to suffer a "Beckmann rearrangement."

CHICAGO, April, 1903.

ON THE OCCURRENCE OF INVERTASE IN PLANTS.

By J. H. Kastle and Mary E. Clark.

Quite recently the attempt has been made in this laboratory to obtain inulase free from other ferments. During our search for a convenient source of this enzyme we have been impressed with the wide distribution of invertase in the vegetable kingdom.

An examination of the literature of the subject revealed that Kosmann[1] had found invertase in the buds and leaves of young trees. In 1886 van Tieghem[2] found this ferment in pollen grains, and later Reynolds Green[3] confirmed these observations and made the further observation that the ferment rapidly increases during germination, particularly if the pollen be germinated on solutions of cane-sugar. Béchamp[4] found it in the petals of flowers, and also in the juice of the mulberry, but failed to find it in the foliage leaves of the plants which he examined. Gonnermann[5] found it in the leaves of the sugar-beet; Atkinson and Kellner[6] in rice; Mieran[7] in the ripe fruit of the banana; and Martinand[8] in crushed grapes, that had been sterilized previous to crushing. Brown and Morris[9] in their interesting contribution to the chemistry and physiology of foliage leaves also record the fact that the air-dried leaves of a species of *Tropæolum* can invert cane-sugar. They did not seem to regard their experiment, however, as absolute proof that the leaf tissue contained invertase, since the inversion of the sugar according to them might have been accomplished by a small amount of fungi growing on and in the leaf. At the same time they point out the desirability of further work in this direction. The latest observations bearing upon this point that have come under our notice are those

[1] Bull. Soc. Chim., **27**, 251 (1877).
[2] Bull. Soc. Bot. de France, **33**, 216 (1886).
[3] Phil. Trans., **185**, B. 385 (1894).
[4] Compt. rend., **59**, 496 (1864).
[5] Bied. Centr., **28**, 550 (1899).
[6] Ztschr. physiol. Chem., **14**, 297 (1890).
[7] Chem. Ztg., **14**, 1283.
[8] J. Chem. Soc. (London). Abs., **80**, II., 35 (1901).
[9] J. Chem. Soc. (London), Trans., 1893, p. 636.

of O'Sullivan.[1] This observer found invertase in the roots, stems, and leaves of the maize, oats, and wheat, and proved that in the case of these plants at least the occurrence of the ferment could in no way be attributed to the presence of micro-organisms.

While, therefore, a good deal had already been done in studying the occurrence and distribution of this enzyme in plants, it seemed that much yet remained to be accomplished, particularly in the way of studying the distribution of the ferment in the several organs and tissues of the plant. Indeed, the results thus far obtained in the present investigation are sufficient to indicate the far-reaching importance of invertase in plant metabolism.

Mode of Procedure and Results.

In searching for the ferment in various tissues, the following mode of procedure has been followed as far as practicable. The portion of the plant under investigation was cut up into fine pieces and thoroughly dried in the air at 40° C. It was then reduced to a fine powder in a porcelain mortar, sometimes alone and sometimes with the addition of a weighed amount of white sand. One-tenth gram portions of the finely powdered tissue were then weighed out and put into small glass bottles, of 70 cc. capacity. To one bottle there was then added 50 cc. of water and 0.5 cc. of toluene, the latter being employed as antiseptic. This served as an active control experiment and enabled us to get an idea of the amount of reducing sugars originally present in the tissue under investigation, or that formed from its own reserve materials during the progress of the experiment. To a second bottle containing 0.1 gram of the tissue there were added 50 cc. of water, 0.5 gram cane-sugar, and 0.5 cc. of toluene, and to a third, 50 cc. of a 1 per cent starch paste and 0.5 cc. of toluene. With certain of the tissues investigated control experiments were also tried, in which 0.1 gram of the tissue was boiled with water and then made up to 50 cc. with the required amount of cane-sugar or starch. In no case, however, did

[1] J. Chem. Soc. (London), Trans., 1960, pp. 691-696.

these control experiments show any increase in the amount of reducing sugars over the quantity present in the active controls, and hence nothing further need be said concerning them. In order to determine whether the ferment was present in the fresh tissue, or formed therein as the result of drying, certain experiments were tried with the freshly macerated tissue. In these experiments somewhat larger quantities of the tissue were employed in order to compensate for the large amounts of water which the fresh tissue contained. The actual amounts employed in such experiments are indicated in the following table. It also occasionally happened that smaller quantities than 0.1 gram of the tissue were employed. This is also indicated in the table.

After standing in the incubator at 38° to 40° C., for the desired interval, usually twenty-four hours, the bottles were removed and 10 cc. of the contents of each boiled with 2 cc. of standard Fehling solution. A comparison of the several experiments of the given series with the active control experiment of that series, as to the amount of reduction, indicated, at least approximately, the inversive and diastatic activity of the particular plant tissue under investigation. Up to this time no attempt has been made to determine accurately the amount of cane-sugar which could be inverted by a given amount of plant tissue. The object has been simply to demonstrate the presence or absence of the ferment.

Up to the present, nineteen different species of plants, representing fourteen different families, have been examined for the ferment. The results are given in the annexed table, together with such experimental data as are required for an understanding of the results.

An examination of the results given in the above table shows that invertase is a ferment of wide, if not universal, occurrence in the vegetable world. It has been found abundantly in every plant thus far examined, and these have been selected in such a way that out of the nineteen different species examined, fourteen different families of plants are represented. It will be seen further that in the several organs of plants invertase is more constant in its occurrence than

No. of experiment.	Name of plant.	Part of plant tested.	Quantity of plant-tissue used.	Result of test with Fehling solution.			
				Active control.	Cane-sugar.	Starch.	Remarks.
			Gram.				
1	White radish, *Raphanus sativus*	Leaves	0.1	Trace of reduction	Good reduction	Good reduction	
2	" " " "	" fresh	0.5	" " "	Complete reduction	Complete reduction	
3	" " " "	Root	0.05	Slight reduction	Nearly complete reduction	" "	
4	" " " "	" fresh	0.5	Distinct "	Good reduction	" "	Starch completely liquefied
5	Red radish	Leaves	0.1	No reduction	Complete reduction	Nearly complete reduction	
6	Carrot, *Daucus Carota*	"	0.1	" "	" "	Trace of reduction	
7	" " "	Root	0.1	Good "	Better reduction than in control	Better reduction than in control	" " "
8	Jerusalem artichoke, *Helianthus tuberosus*	Leaves	0.1	No "	Good reduction	No reduction	
9	" " " "	Tubers, young	0.1	Distinct reduction	Complete reduction	Same as control	
10	" " " "	" " fresh	0.5	Slight "	" "	Not tried on starch	
11	" " " "	" old, dry	0.05	" "	Good reduction	Slightly more than control	
12	Potato, *Solanum tuberosum*	Leaves	0.1	" "	Complete reduction	Good reduction	
13	" " "	Tubers, very young, just forming	0.03	No reduction	Good reduction	No reduction	
14	" " "	" young	0.05	" "	" "	" "	
15	" " "	Old tuber, sprouted, part near sprout	0.05	" "	Some "	" "	
16	" " "	Sprout	0.01	" "	Complete reduction	Slight reduction	
17	" " "	" fresh	0.5	Good reduction	" "	Good "	Tested after standing 4 hours at 40° C.
18	Experiment 17 continued	" "	0.5	" "	" "	Larger reduction than control	Time, 21 hours
19	" " "	Tuber, very small, just forming	0.01	No reduction	Good reduction	No reduction	" 7 days at 40° C.
20	" " "	" young, ¼ inch in diameter	0.05	" "	" "	" "	" 7 " " " "
21	*Dahlia variabilis*	Leaves	0.1	" "	Complete reduction	Complete reduction	
22	" "	Bulbs	0.1	Trace of reduction	Slight "	Slight "	
23	Dandelion, *Taraxacum officinale*	Leaves	0.1	No reduction	Complete "	" "	
24	" " "	Roots	0.1	" "	Good reduction	" "	
25	Onion, *Allium cepa*	Bulb, old	0.1	Trace of reduction	Trace of reduction	Trace of reduction	
26	" " "	" "	0.1	" " "	No reduction	No reduction	
27	" " "	Sprouts, from old bulb	0.1	Good reduction	Complete reduction	Nearly complete reduction	
28	*Spirogyra*,	Entire plant	0.035	No "	Some reduction	No reduction	
29	" Experiment 28 continued		0.035	" "	Good "	Slight reduction	
30	*Sorghum vulgare saccharatum*	Young plant, entire	0.1	Slight "	Complete reduction	Complete reduction	
31	Sugar-beet, *Beta vulgaris*	Leaves	0.1	No "	" "	" "	
32	" " " "	Root	0.1	Distinct reduction	Good reduction	Some reduction	
33	Maize, *Zea Mays*	Seedling, stem and leaves	0.1	" "	Complete reduction	Complete reduction	
34	" " "	" roots	0.1	" "	" "	" "	
35	" " "	Large plant, leaves	0.1	Trace of "	Nearly complete reduction	" "	
36	" " "	" " roots	0.1	Distinct "	Complete reduction	" "	
37	" " "	" " stalk	0.1	Good "	" "	" "	
38	" var. sugar corn	" " leaves	0.1	Distinct "	Good reduction	Nearly complete reduction	
39	" " " "	" " roots	0.1	" "	Slightly more than control	Good reduction	
40	" " " "	" " stalk	0.1	Good "	Good reduction	" "	
41	" " " "	Grain, unripe	0.05	Distinct "	Nearly complete reduction	Nearly complete reduction	Starch liquefied
42	" " " "	" "	0.05	" "	Complete reduction	Complete reduction	" "
43	Annual Wormwood, *Artemisia annua*	Leaves	0.1	Trace of "	" "	" "	" rapidly liquefied
44	Pine, species not determined	"	0.1	Slight "	" "	Slightly more than control	
45	Grape, cultivated, Ives Seedling	Fruit, unripe	0.1	" "	" "	" " " "	
46	Hemp, *Cannabis sativa*	Root	0.1	" "	Good reduction	Somewhat more than control	" liquefied
47	" " "	" of plant infected with broom rape	0.1	No reduction	Complete reduction	Good reduction	" "
48							
49	Soy-bean, *Glycine hispida*	Leaves	0.1	" "	" "	Complete reduction	All starch liquefied
50	" " " "	Tips of growing stem	0.1	Slight reduction	" "	" "	
51	" " " "	Pod, with forming seeds	0.1	" "	" "	" "	
52	" " " "	Root	0.1	No reduction	Good reduction	" "	
53	Broom-rape, *Orobanche ramosa*	Entire plant	0.05	Very slight red'ct'n	Complete reduction	Slight reduction	
54	" " " "	Seed pod	0.05	No reduction	" "	" "	
55	" " " "	Entire plant, very young, fresh tissue	0.5	Good "	" "	More reduction than control	
56	" " " "	Enlarged bulbous portion at base of full-grown plant	0.5	Trace of reduction	" "	Scarcely more than control	
57	" " " "	Roots, fresh	0.25	No reduction	" "	No reduction	
58	" " " "	Seeds, yellow, fresh	0.03	" "	" "	Not tested on starch	
59	" " " "	" " dried in air	0.03	" "	" "	" " " "	
60	" " " "	" " " at 40° C in air	0.04	" "	" "	Slight reduction	
61	" " " "	" brown, ripe, air-dried	0.03	" "	Good reduction	Not tested on starch	
62	Sweet potato, *Ipomœa Batatas*	Leaves, young, near tip of vine	0.1	Slight reduction	Complete reduction	Nearly complete reduction	
63	" " " "	" mature	0.1	No reduction	" "	Complete reduction	
64	" " " "	Tubers, young, fresh	0.5	Slight reduction	Good reduction	" "	
65	Locust, *Robinia Pseudacacia*	Stem	0.1	No reduction	Some "	Good reduction	Starch partly liquefied
66	" " "	Root	0.1	Slight reduction	More reduction than control	Complete reduction	" completely liquefied
67	" " "	Leaves, young, near tip of branch	0.1	Trace of reduction	Complete reduction	" "	
68	" " "	Leaves, mature	0.1	" " "	Nearly complete reduction	Some reduction, more than control	

diastase. Contrary to the views and results of Béchamp, invertase occurs abundantly in the leaves of plants, and his failure to find it in the leaves of the locust, *Robinia Pseud-acacia*, is probably to be ascribed to the fact that he attempted to prepare clear aqueous extracts of the ferment, whereas, except under great pressures, this is impossible in many cases. The same difficulty was experienced by Wortmann[1] in attempting to extract diastase from foliage leaves, and yet it has been conclusively proven by Brown and Morris[2] that the leaves of most, if not all, of the starch-forming plants contain this enzyme.

In the second place, it will be observed that invertase occurs in the plant in some rather unexpected associations. It has been found, for example, in the growing tubers of the potato and the artichoke, and also in the sprouts of the potato. Now, as inulin is the chief reserve material of the artichoke and starch that of the potato, one would naturally be inclined to expect the occurrence of relatively large amounts of inulase and diastase, respectively, in these young tubers, and also that of diastase in the sprout of the potato, and while these ferments are present in these organs of these plants, they are not present in such quantities as invertase, or at any rate cane-sugar is much more easily hydrolyzed by these tissues, under antiseptic conditions, than inulin or starch.

Thirdly, it will be observed that invertase is not confined to those plants which store up cane-sugar as the characteristic reserve material. On the contrary, while it has been found in such of these as have thus far been examined, *viz.*, the sorghum plant and sugar-beet, it has also been found abundantly in those plants which store up starch and inulin as reserve materials, and what is of still greater interest, it has been found in those very organs of the plant that are actively engaged in storing up starch and inulin, for example, in the growing tubers of the potato and artichoke and in the unripe grain of the maize. It is our intention to investigate more fully the occurrence of invertase in the reserve organs of these plants in the hope of learn-

[1] Bot. Ztg., 1890, p. 583.

[2] J. Chem. Soc. (London), Trans., 1903, pp. 604-677.

ing something further as to the part played by this ferment in the storing up of starch and inulin.

The fact that invertase and cane-sugar are both of such general occurrence in plants is sufficient in itself to indicate the extreme inportance both of this carbohydrate and this ferment in plant metabolism. Curiously, two exactly opposing views have been held regarding the origin and fate of cane-sugar in the plant. As the result of his studies on the occurrence and products of alteration of cane-sugar in plants, Kayser[1] reached the conclusion that this carbohydrate results from starch by the direct action of a diastatic ferment, and that it is then transformed into invert sugar by the action of a ferment similar to invertin, before it is consumed in the respiratory processes in the plant. On the other hand Brown and Morris,[2] ten years later, arrived at the conclusion that the starch formed by the chloroplasts is not, strictly speaking, autochthonous, but that it owes its origin to cane-sugar. According to these observers, cane-sugar is antecedent to starch and is probably the first product of photo-synthesis. According to them it serves as a temporary reserve material and is probably to be regarded as the starting-point in all of the metabolic changes taking place in the leaf.

The fact that invertase occurs so generally in foliage leaves and that it is so widely disseminated throughout the several organs of the plant, lends additional support to the views advanced by Brown and Morris, and the fact that it is also largely present in the reserve organs of the plants storing inulin as well as those storing starch, would seem to point to cane-sugar as the substance immediately antecedent not only to starch but to other reserve materials as well. It is known that, generally, any particular stereo-configuration on the part of a compound is preserved in its derivatives. Such being the case, and since, further, the molecule of cane-sugar is made up of a dextro- and a laevo-portion, it is readily conceivable that such optically active reserve substances as starch and inulin are produced from it, first by its conversion into invert

[1] Versuchsstationen, 29, 460-473 (1883).
[2] J. Chem. Soc. (London), Trans., 1893, p. 673.

sugar through the action of invertase and the subsequent polymerization of dextrose and levulose. The further fact that the simpler sugars resulting from the hydrolysis of cane-sugar belong to the aldose and ketose types, respectively, would seem to lend additional probability to the view that all of the more complex carbohydrates are derived originally from cane-sugar. The production of cane-sugar by the plant as the first temporary reserve material becomes readily intelligible on the supposition that *d*-glucose, *l*-glucose, *d*-levulose, and *l*-levulose are the first products of photo-synthesis, and that two of these, *viz.*, *l*-glucose and *l*-levulose are at once consumed to supply the immediate needs of the plant. *d*-Glucose and *d*-levulose might then go on accumulating in the cell until a certain concentration was reached when, under the influence of invertase, they would combine to form cane-sugar. This latter compound, then, would sustain to the plant the relation of a temporary reserve material to meet its more remote requirements or to be transformed into still more complex, less readily hydrolyzable reserve materials, such as starch and inulin, as the case might be. We are aware that the idea that the racemic forms of optically active compounds are always the first products of plant synthesis, is not shared by all chemists. It is worthy of note, however, that racemic compounds, as well as their active components, do occur in plants, and that certain of the fungi and micro-organisms display a selective action in the appropriation of optically active compounds as foods, thereby enabling us oftentimes to obtain optically active compounds from the racemic form.

With the view of throwing further light on these interesting questions we hope, if the necessary materials can be secured, to make a thorough study of the conduct of the racemic forms of glucose and levulose towards the hydrolyzing enzymes and certain fungi and higher parasitic plants.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, August, 1903.

ON A NEW METHOD FOR THE PREPARATION OF PURE IODINE.

By Launcelot W. Andrews.

The impurities to be looked for in iodine are moisture, hydriodic acid, bromine, chlorine, and cyanogen iodide. A number of processes have been suggested for obtaining a product free from these contaminations, among which may be mentioned the methods of Stas,[1] Wittstein,[2] Mohr,[3] Meineke,[4] and of Lean and Whatmough.[5] All these methods are either very elaborate, demanding no inconsiderable sacrifice of time, or, like the simple resublimation of iodine with potassium iodide, are inefficient. The reaction between fused potassium pyrochromate and potassium iodide, which occurs in accordance with the equation

$$5K_2Cr_2O_7 + 6KI = 8K_2CrO_4 + Cr_2O_3 + 6I,$$

seemed to offer a possible and simple method for obtaining pure iodine directly from the impure iodide. A preliminary experiment showed that by fusing a mixture of 29.5 grams of potassium pyrochromate with 20 grams of potassium iodide, practically the whole of the iodine was obtained in the free state. No iodine was set free on fusing a mixture of normal potassium chromate and iodide. A mixture of potassium bromide (6 mols.) with pyrochromate (5 mols.) furnished, on fusion, a trace of free bromine, but when to the same mixture a little normal potassium chromate had been added, no bromine was set free. It should be said that all mixtures were made by rubbing the constituents thoroughly together in a mortar.

These experiments made it appear almost certain that if potassium iodide and pyrochromate were mixed together, with the former in moderate excess of the amount required by the equation, a product free from bromine and chlorine would be assured. Accordingly, 28 grams of potassium pyrochromate

[1] Nouvelles Recherches sur les Lois des Proportions Chimiques, p. 136.
[2] Dingler's Poly. Jour., 200, 310 (1871).
[3] Titrir-Methode, 1874, p. 269.
[4] Chem. Ztg., 16, 1219 (1892).
[5] J. Chem. Soc. (London), 73, 148 (1898).

were powdered with 20 grams of potassium iodide and 1 gram of potassium bromide and the mixture was fused in a wide, glass tube. Three and eight-tenths grams of the sublimate were tested in the following manner for bromine: The iodine was thrown into 100 cc. of hot concentrated ammonia and a slight excess[1] of silver carbonate was added and the solution filtered. From the filtrate the silver was precipitated by hydrogen sulphide and the liquid boiled down to a very small bulk with a little pure barium carbonate. The residue gave no reaction for bromine, either by the fluorescein test or on spectroscopic examination according to Lecoq de Boisbaudran.[2]

To summarize, the following are the necessary steps in the preparation of pure iodine by the method given: Pulverize potassium iodide with one and four-tenths times its weight of potassium pyrochromate, each salt having been, previously, separately fused to insure perfect dryness. Introduce the thoroughly incorporated mixture into a wide tube, closed at one end, and heat to about 200° in a current of dry air to expel any moisture which may have been taken up during the pulverization. Place a plug of dry glass wool over the mixture and wipe out carefully the interior of the tube above the plug with absorbent cotton secured to a glass rod. Slip over the open end of the tube a second, short one, fitting it as snugly as possible. Fix the tube at an angle with the horizontal and heat the powder gradually with a small flame, using, if necessary, a screen of asbestos board. Having sublimed the iodine into the upper part of the tube, cut off the latter, when cold, at a point 2 or 3 cm. above the glass-wool plug, or, if smaller amounts are being operated on, the tube can be melted off at the place indicated.

CHEMICAL LABORATORY,
STATE UNIV. OF IOWA,
July 6, 1903.

Since sending the foregoing communication to the editor of the AMERICAN CHEMICAL JOURNAL, it has come to my

[1] Ascertained by acidifying a filtered sample with hydrochloric acid.

[2] Compt. rend., 91, 902 (1881). This method rests on the observation of barium bromide lines at wave lengths, 535.8 and 520.6

knowledge through the last number of the *Central-blatt* (**1**, 1435 (1903)) that L. L. de Koninck has published in the *Bulletin de l'Académie royale Belgique*, **17**, 15, a nearly identical method for the preparation of pure iodine. The priority, accordingly, belongs to him, but in view of the importance of the subject, it still appears worth while to publish the entirely independent confirmation of his results which my experiments afford; the more so since, so far as it is possible to judge from the abstract, his work does not directly demonstrate that the process can be so conducted as to insure the preparation of a product free from bromine.

CHEMICAL LABORATORY,
STATE UNIV. OF IOWA,
July 25, 1903.

Contributions from the Sheffield Laboratory of Yale University.

CXIII.—ON IODOCYANIDES OF POTASSIUM AND CAESIUM.

BY C. H. MATHEWSON AND H. L. WELLS.

By dissolving iodine in concentrated solutions of potassium cyanide, Langlois[1] prepared a compound to which he gave a formula corresponding to $KI.4CNI.4H_2O$. Since this salt does not correspond to the alkali-metal trihalides or pentahalides, examples of which are $KCl.ICl$ and $KCl.ICl_3$, we have undertaken a new examination of Langlois' compound, and, having found that his formula was correct, except in regard to the amount of water in it, we have attempted to prepare caesium iodocyanides, which, in view of the great stability of the caesium perhalides, promised to be more stable than the rather unsatisfactory potassium compound. As the result of the latter investigation, we have obtained the single compound $CsI.2ICN$, which does not correspond to the potassium salt, but which may, perhaps, be regarded as showing analogy to the pentahalides, although no crystallographic resemblance to any of the latter could be made out by Professor Penfield, who kindly examined the crystals.

Potassium Iodocyanide, $KI.4CNI.H_2O$.—This compound was prepared by dissolving varying proportions of iodine in con-

[1] Ann. chim. phys. [3], **60**, 220 (1860).

centrated potassium cyanide solutions and also by adding large amounts of potassium iodide, together with iodine, to such solutions. No evidence of the existence of any other combination of potassium iodide and cyanogen iodide was found. The compound forms small, colorless needles, as described by Langlois. The substance is very unstable, giving off cyanogen iodide when exposed to the air, so that it was necessary to press it rapidly on paper for analysis. The following analyses were made of different products:

	Calculated for $KI.4CNI.H_2O$.	Found. I.	II.	III.
K	4.91	5.64	5.65	5.54
I	79.76	79.62	79.44	79.20
CN	13.06	12.48	12.24	12.59
H_2O(diff.)	2.26	2.26	2.67	2.67

It appears certain that Langlois obtained too much water in the compound, probably from insufficient drying. In fact, it seems quite possible that the substance is anhydrous, since our products could not be air-dried, and since the amount of water corresponding to 1 molecule is small.

Potassium was determined by carefully heating the compound and weighing the potassium iodide. Cyanogen was determined volumetrically with silver nitrate, after decolorizing the aqueous solution of the substance with sulphurous acid, and then making the liquid ammoniacal. After a permanent precipitate of silver iodide had appeared, indicating the end of the titration for cyanogen,[1] an excess of silver nitrate was added, the resulting precipitate was collected on a filter, extracted with ammonia, and the residual silver iodide was weighed in order to determine iodine.

Caesium Iodocyanide, $CsI.2ICN$.—This compound forms cinnamon-colored, orthorhombic plates, which are rather sparingly soluble in water. It is much more stable than the potassium compound, but still it gives off an odor of cyanogen iodide. It was prepared by dissolving iodine in caesium cyanide solution, but more conveniently, on account of the difficulty of preparing caesium cyanide, by dissolving caesium iodide and cyanogen iodide in warm water and cooling.

[1] Denigès: Ann. chim. phys. [7], **6**, 381.

Caesium triiodide was almost invariably deposited after the iodocyanide had formed, but there was no difficulty in getting out the crystals of the latter in a satisfactory condition. Seven crops were prepared under the following conditions:

	I.	II.	III.	IV.	V.	VI.	VII.
CsI, grams	10	10	10	5	2.5	1	1
CNI, "	1	2	5	5	5	5	10

In each case the solution in water was about 25 cc. in volume. These gave the following analyses:

	Calculated for CsI.2CNI.	Found. I.	II.	III.	IV.	V.	VI.	VII.
Cs	23.50	23.57	....	....	28.59	....	....	23.41
CN	9.18	9.03	9.12	9.20	9.31	9.30	9.18	9.24
I	67.31	67.65	....	67.88	....	68.15	....	67.53

It is evident from these results that only a single compound is formed under widely varying conditions.

The methods used for the analysis of this salt were similar to those used for the potassium compound.

NEW HAVEN, CONN., June, 1903.

Contributions from the Sheffield Laboratory of Yale University.

CXIV.—ON A COMPOUND OF MERCURIC CYANIDE AND CAESIUM IODIDE.

BY C. H. MATHEWSON AND H. L. WELLS.

It has been found by one of us[1] that mercuric iodide and caesium iodide form a series of five double salts, and that the two chlorides form the same number of compounds, while mercuric iodide and caesium chloride give only a single double salt, $Cs_3HgCl_2I_2$. The present investigation has been undertaken in order to find out how mercuric cyanide and caesium iodide would behave in the formation of double salts, and the results show that these salts combine in only one proportion, forming the compound $CsI.Hg(CN)_2$.

It is to be noticed that this double salt belongs to a different type from that of the chloriodide, but the point appears to be established that the presence of two different acid radicals prevents the formation of a variety of compounds. It is well

[1] Am. J. Sci., 44, 221 (1892).

known that mercuric cyanide combines with many other salts, and hence it shows a remarkable tendency toward double-salt formation, but in spite of this tendency, and in spite of the facility with which caesium salts form double compounds, only a single double salt is formed in this case.

The salt under consideration was prepared by cooling solutions containing caesium iodide and mercuric cyanide in proportions by weight varying from 1 : 15 to 10 : 1. When more than 15 parts of mercuric cyanide to 1 of caesium cyanide were used, either indefinite mixtures or crops of nearly pure mercuric cyanide were obtained. The double salt forms thin, white, pearly plates, which can scarcely be distinguished in appearance from pure mercuric cyanide. The salt is readily recrystallized from water, and thereby remains unchanged in composition. Acids decompose the salt with evolution of hydrocyanic acid and formation of mercuric iodide.

The following analyses were made of different crops :

	Calculated for $CsI.Hg(CN)_2$.	Found. I.	II.	III.	IV.	V.	VI.
Cs	25.97	25.40	25.81	25.58	25.87	25.66	25.40
Hg	39.06	39.67	39.17	39.13	39.09	....	....
I	24.80	24.48	24.69	24.70	24.63	....	....
CN	10.15	....	....	....	9.80	....	....

NEW HAVEN, CONN., July, 1903.

REVIEWS.

BRIEFWECHSEL ZWISCHEN J. BERZELIUS UND F. WÖHLER, IM AUFTRAGE DER KÖNIGL. GESELLSCHAFT DER WISSENSCHAFTEN ZU GÖTTINGEN. Mit einen Commentar von J. VON BRAUN. Herausgegeben von O. WALLACH. Erster Band mit Berzelius' Bildniss. pp. xxii + 718. Zweiter Band mit Wöhler's Bildniss. pp. 744. Leipzig : Verlag von Wilhelm Engelmann. 1901.

This important work should have been reviewed long ago. It ought to be read by every chemist. It reveals to us the characters of the two great men as nothing else could at this time. The letters cannot be abstracted. They must be read from beginning to end. This requires time, but the time will be well spent.

Some years ago, in view of the occurrence of the hundredth anniversary of Wöhler's birth, July 31, 1900, the Royal Society of Sciences in Göttingen planned to publish this correspondence if Wöhler's letters to Berzelius could be secured.

These were left to the Swedish Academy of Sciences. Fortunately, the Academy gave its consent to the publication. Wöhler had carefully preserved the letters of Berzelius, and had placed them in charge of the Swedish Academy, on condition that they should not be published before January 1st, 1900.

The correspondence began in 1823, when Wöhler asked to be admitted into Berzelius' laboratory, and ended in 1848 with the death of Berzelius. This is an extremely important period in the history of chemistry. Professor Wallach, the editor, says: "It is intended by this publication to facilitate the study of one of the most interesting chapters of chemical research and to lead the younger chemists to trace to their sources the important investigations from which our present chemistry has sprung. Nothing could be more profitable for the healthy development of our science than for the young chemists, who are just coming to the front, to accustom themselves to look backward out of the turbulence of the present and to get thoroughly under the influence of the thoughtful and almost painfully thorough investigations which stamped the time of Berzelius and Wöhler as the classic age of chemistry."

As is well known, after Wöhler's return to Germany from Sweden, he soon began the translation of the great Lehrbuch of Berzelius and also of Berzelius' Jahresbericht. This work he kept up until the death of Berzelius. The Lehrbuch filled ten large volumes and five editions were issued, though the fifth was not finished. This literary work alone was the work of a giant. Few men have done as much. But the most important work of both Berzelius and of Wöhler was that of teaching and investigating. Both of them contributed enormously to the advancement of chemistry. How they could have done the amount of work they did without breaking down it is, at first sight, difficult to see. And yet, after reading this correspondence, the explanation appears. *They kept at it.* They rarely forgot their work. Occasionally they grew weary and talked of giving it up, but they did not give way to their impulses, and to the end they kept in harness. Even after it became impossible for Berzelius to write, he dictated letters about the Lehrbuch, the Jahresbericht, and his relations to Liebig.

Every chemist who thinks he is overworked ought to study the life of Berzelius. To be sure, probably but few could stand the strain that he subjected himself to, but there is a large margin between the day's work of the average chemist and the day's work of Berzelius or of Wöhler.

Much of the correspondence has to deal with details touching the Lehrbuch and the Jahresbericht. Typographical errors, nomenclature, arrangement, cuts, etc., are the chief topics of many of the letters, but, as the editor remarks in the preface, any attempt to condense these letters would have taken away from the clearness of our view into the scrupulous care with which Berzelius dealt with such matters.

In order to make the references of the writers to chemical topics clear, Dr. J. von Braun has appended notes that will be of great aid in enabling younger chemists to understand the significance of many passages in the letters that would otherwise be more or less obscure. These are clearly written and show a thorough grasp of the subject.

The writer of this notice has marked throughout the two volumes many especially striking paragraphs. It would be interesting here to quote these with or without comment, but on looking through the book he finds that they would fill many pages and only a few can be given. Vol. II., page 79, Wöhler writes: "Dann habe ich Dir meinen Dank zu sagen für Deinen Brief von 28 Dec. und das damit gekommene Thierchemie-Manuscript. Das gibt wieder ein gutes Stück Arbeit. Bei der wenigen Zeit, die mir dazu übrig bleibt, würde ich den Muth verlieren hätte ich nicht Dich als Muster des unbegreiflichsten Fleisses vor Augen, sähe ich nicht, welch ganz andere und viel grössere Arbeit Du mit der Ausarbeitung des Originals hast, als ich mit der Uebersetzung habe. Doch ich fürchte, diese Jeremiaden über Zeitmangel habe ich schon mehr als einmal vorgebracht. Verzeihe dass ich wiederholt Dich damit schwäche. Inzwischen entspringen sie auch aus dem betrübten Gefühl, dass ich für das was mir am Meisten am Herzen liegt für meine eigenen Arbeiten so gut wie keine Zeit übrig behalte, dass ich die Minuten dazu stehlen muss, dass in einer so zerstückten und zerstreuten Zeit keine Untersuchungen zu Stande kommen können. Diese Klagen sollen also zugleich vor Dir als Entschuldigungen gelten, dass ich nicht so productiv bin, als Du von mir erwartest."

Vol. II., p. 134, Berzelius writes: "Es muss in wissenschaftlicher Hinsicht ein Etwas geben ähnlich dem, was man in socialer Takt nennt, ein Gefühl das, ohne dass man für den Augenblick sich die Gründe dafür klar macht einem sagt, was zu thun sich nicht schickt oder was angeht, und welches Gefühl einige in hohem Grade besitzen und andere, wenn sie auch mit noch mehr Genie als diese begabt sind, ganz und gar entbehren. Wenn ich eine unrichtige theoretische Darstel-

lung sehe, so fühle ich es, auch wenn die richtige mir unbekannt ist, ohne es mir noch klar machen zu können, dass sie falsch ist, so wie das Ohr einen falschen Ton hört. Und wenn eine richtige Darstellung kommt, so wird sie sofort erkannt, sie erfreut und macht einen angenehmen Eindruck, so wie eine reine Intonation. Etwas ähnliches muss auch in der Wissenschaft mit im Spiele sein, denn wir sind in vielen Dingen wie Maschinen, und was ein jeder von uns in richtiger Spekulation vermag oder nicht vermag, beruht ganz und gar auf der verschiedenen Organization unserer Gehirne. Der Versuch, demjenigen einen Begriff von schöner Musik zu geben, der den Unterschied zwischen falschen und reinen Tönen nicht hört, ist ebenso vergeblich wie denjenigen, der nicht angeborenen Takt besitzt, in Opinionsachen zu überzeugen. Er kann, falls er nicht voreingenommen ist, das richtige als Gedächtnisaufgabe lernen, aber er ist immer bereit, es gegen anderes auszutauschen, denn er empfindet nicht, dass dieses weniger richtig ist.—Oder—ist dieses nur eine dumme Idee von mir?"

It appears from a passage in a letter written by Wöhler, April 25th, 1840 (Vol. II., p. 169), that the well-known satire on the substitution theory that was published in the Annalen (Bd. **33**, 308) was written by Wöhler. Liebig published it without consulting the writer. Wöhler says in regard to this: "Dass Dir der Einfall über die Substitutions-theorie nicht missfallen hat und dass Du bemerkst, er verdiene allgemeiner gelesen zu werden, ist mir eine wahre Beruhigung gewesen, da Liebig ihn, ohne mein Wissen und Willen, aber versteht sich ohne meinen Nahmen, wirklich drucken lassen, indem er ihn in dem einen und anderen Punkt etwas abgeändert und einige neue Witze hinzugefügt hat. Ehe ich nämlich den Brief, worin ich Dir den Spass geschrieben hatte, zumachte, kam ich auf den Einfall, denselben auch, weil er mir selbst gefiel, Liebig mitzutheilen und für ihn in Form eines aus Paris datirten Briefes abzuschreiben, ohne dass ich aber im Entferntesten daran dachte, dass er so toll sein würde ihn in den Annalen abdrucken zu lassen. Er ist mit S. Ch. Windler (Schwindler) unterzeichnet."

On page 267, Vol. II., occurs this advice to Wöhler: "Lieber Wöhler, arbeite tüchtig so lange Du noch Kräfte hast, denn Du glaubst nicht, was der Mensch für ein Vieh wird, wenn er zu altern anfängt." Berzelius was then in his 62nd year.

In 1841 (Vol. II., p. 274) Wöhler writes in regard to the work of translation to which he gave so much time: "Für

Niemand Anderes in der Welt als für Dich würde ich dieses Geschäft noch einmal übernehmen. Es ist nur Gefühl des Dankes und der Pflicht, nur Pietät gegen Dich, die mich dazu bestimmt."

Berzelius' relations to Liebig are illuminated by these letters. They respected each other and at times were positively affectionate, but at times they were quite the opposite. In 1842, Berzelius really thought Liebig was becoming insane, and writes (Vol. II., p. 298): "Liebster Wöhler! Ich schreibe Dir dieses in grosser Traurigkeit. Ich erhielt mit der letzten Post das Märzheft der Annalen, das ich am Sonntag auf dem Lande, wo ich nichts anderes zu thun hatte, durchlas und woraus ich nun deutlich ersehe, dass meine im letzten Briefe geäusserte Befürchtung, dass Liebig nahe daran sei, den Verstand zu verlieren, früher, als ich dachte, zur Wirklichkeit geworden ist und dass er nun das, was wir auf Schwedisch "galen" nennen, wirklich ist. Was soll man mit dem armen Manne thun? Wenn seine Freunde sich jetzt nicht um ihn bemühen, so kann er leicht unrettbar verloren gehen."

Wöhler defends Liebig warmly, while acknowledging that there appears to be some justification for the statements. He says, Vol. II., p. 301: "Es ist ein durchaus rechtlicher, ehrenhafter und nobeler Charakter, aber leidenschaftlich, unbesonnen und rücksichtslos. Ich missbillige im höchsten Grade diese Rücksichtslosigkeit, diese unwürdige Art der Polemik, diese anmaasliche Sprache in wissenschaftlichen Gegenständen; aber ich liebe ihn als einen meiner besten Freunde und verehre ihn als einen ausgezeichneten Geist."

Side lights are thrown upon the scientific partnership between Liebig and Wöhler. Berzelius has advised Wöhler to withdraw. To this Wöhler replies (Vol. II., p. 324): "Da ich von Liebig rede, will ich hier gleich die Bemerkungen in Deinem Brief von 9ten Aug., das gemeinschaftliche Arbeiten mit ihm betreffend, beantworten. Ich muss Dir im Allgemeinen beistimmen und anerkennen dass ich mit meinem Theil Ehre, unverdienterweise, etwas zu kurz komme. Aber was liegt daran, wenn die Sache an sich dadurch gewinnt, und dass ist ganz gewiss der Fall. Wir beiden, Liebig und ich, haben ungleiche Arten von Talent, die, zusammenwirkend, einander ergänzen und etwas zu leisten vermögen. Niemand erkennt diess mehr an als Liebig selbst, und Niemand lässt mir für den Antheil an unseren gemeinschaftlichen Arbeiten mehr Gerechtigkeit widerfahren als er, wenigstens privatim. Uebrigens wenn ich auf die öffentliche Meinung einen Werth

legen will, so wäre es, sollte ich denken, unklug gehandelt, gerade jetzt mich von ihm zurückzuziehen und aufzuhören, Arbeiten gemeinschaftlich mit ihm auszuführen. Doch ist diess nicht der Grund, warum ich ihm die Narcotin-Untersuchung zum Gegenstand einer gemeinschaftlichen Arbeit angeboten habe (was schon vor Empfang Deines Briefes von 9ten Aug. geschehen war). Es geschah diess, um ihm einen thätlichen Beweis meiner unveränderten Freundschafts-Gesinnungen gegen ihn zu geben, zu einer Zeit, wo von allen Seiten (zum Theil verdiente) Verdriesslichkeiten auf ihn losstürmten und er in diesem Zustande von Gereiztheit Gründe und Symptome zu sehen glaubte, dass auch ich ihn verleugnen und verlassen wollte."

The publication of the results of work done by a student under the direction of his teacher is touched upon in a letter from Wöhler (Vol. II., p. 395): "Da nun in neuerer Zeit häufig der Fall vorkommt dass nicht unwichtige Arbeiten von Eleven auf Veranlassung und unter Leitung ihrer Lehrer vorgenommen und dann die Resultate in den Lehrbüchern erwähnt werden, so kann oft die Frage enstehen, wessen Nahmen dabei als Autorität zu nennen ist. Dabei immer die Explication zu geben, dass es unter der Leitung von dem und dem geschehen sei, ist zu umständlich und passt nicht wohl für ein Lehrbuch. Für diese Fälle scheint mir daher der Ausweg, den Du einmal angewendet hast, im Allgemeinen der beste zu sein, nämlich die Arbeit als eine gemeinschaftliche des Lehrers und der Eleven anzuführen. So wäre also die obige Arbeit über die Wirkung des Chlors auf das Kohlensulfid als 'von Wöhler und Kolbe' zu bezeichnen. Ich hoffe, dass Du mir diese Bemerkung nicht als eine kleinliche Eitelkeit auslegen wirst."

To this Berzelius remarks (Vol. II., p. 401): "Es muss dort Wöhler und Kolbe richtig eingetragen werden; was Deinen Vorschlag betrifft in allen ähnlichen Fällen auf dieselbe Weise zu verfahren, so ist das wohl im Grunde das Richtige, aber was soll ein armer Kompilator machen, wenn er seinen Honig aus einem Journal holt, wo nur der Schüler als Verfasser angegeben ist. Das richtigste ist, ihn dadurch zu autorisieren, dass die Namen des Lehrers und des Schülers bei dem Artikel im Journal zusammenstehen. Einen solchen "blanc-bec" in seinem eigenen Namen ausfliegen zu lassen, verwöhnt so sehr, dass er stolz und eitel und anspruchsvoll wird. Dein Völckel z.B., wenn man das, was er unter der Leitung von Deiner Hand und von Deinem Kopfe hinsichtlich der Schwefelcyanverbindungen gemacht hat, mit dem vergleicht, was er

jetzt nachher auf eigene Faust und nach seinem eigenen Kopfe gemacht hat, welch ein Unterschied! und doch welche Ansprüche in der Art der Darstellung, er behandelt Liebig wie eine Prise Schnupftabak. Ich rate Dir desshalb nunmehr damit anzufangen, Deinen Namen neben den des Schülers auf solche Arbeiten zu setzen, zu denen Du in dem Laboratorium, dem Du vorstehst, die Anleitung giebst. Es bleibt immer eine Wahrheit das die Sache Dir gehört und die Arbeit dem Schüler."

But these few extracts must suffice. It is hoped that every earnest young chemist will carefully read the whole of the correspondence. He cannot fail to be interested and benefitted. Older chemists need no advice. I. R.

THE TEACHING OF CHEMISTRY AND PHYSICS IN THE SECONDARY SCHOOL. By ALEXANDER SMITH, B.Sc., PH.D., Associate Professor in the University of Chicago, and EDWIN H. HALL, PH.D., Professor in Harvard University. New York, London, and Bombay: Longmans, Green & Co., 1902. pp. xiii + 377.

It would be well if every teacher of chemistry and of physics should not only read, but carefully study, this book. It is full of good common sense presented in an attractive way. It does not attempt to tell the teacher exactly what to do under all circumstances, but it does offer a great many valuable suggestions in a kindly and practical way. Neither author assumes the "high and mighty" attitude towards his readers. They show that they have lived and suffered, but that they have kept their eyes open and have learned something about teaching.

The first part, that which deals with chemistry, consists of eight chapters. These bear the headings: I. Introduction; II. Chemistry in the Curriculum; III. The Introduction of the Subject; IV. Instruction in the Laboratory; V. Instruction in the Classroom; VI. Some Constituents of the Course; VII. The Laboratory, Equipment, and Illustrative Material; VIII. The Teacher, His Preparation and Development.

The second part (pages 233 to 371) contains thirteen chapters with the following titles: I. Whether to be a Teacher of Physics; II. Preparation for Teaching; III. The Teacher as Student, Observer, and Writer; IV. Problems of Laboratory Practice; V. School Text-books of Physics; VI. Discovery, Verification, or Inquiry?; VII. The Technique of Laboratory Management; VIII. Lectures and Recitations; IX. Physics in Primary and Grammar Schools; X. Physics in Various Kinds of Secondary Schools; XI. On the Presentation of Dynamics; XII. Plan and Equipment of a Laboratory; XIII. Physics Teaching in Other Countries.

In his preface, Professor Smith says: "The book assumes the reader's familiarity with the science. Many brief references to chemical matters would have been greatly expanded or carefully limited if they had been intended for beginners. There has been no intention to recommend particular text-books. Many have been cited as possessing some point of special excellence, but this must not be taken to indicate emphatic approval of those works as wholes, say for use with a class of beginners."

In respect to advice about books, the authors have both been so extremely tolerant that the teacher will get the impression that any one of a dozen or more text-books will answer about as well as any other, though he will also get the impression, perhaps a proper one, that no matter what book he may choose he will probably wish that he had chosen another.

Professor Smith restates a fundamental truth that is never to be lost sight of when he says: "In all instruction the personality of the teacher is held to be a factor of not less importance than the nature of the subject taught. The close personal contact which laboratory instruction secures between the pupil and teacher, and the consequent greater opportunity which his personality has to impress itself upon the pupils is not one of the least of the benefits we are discussing."

Further, he says (p. 122): "One of the most serious faults of much chemistry teaching is that the pupils are allowed to work by themselves in the laboratory in the absence of the teacher." * * * "The disastrous blunder of permitting or encouraging unsupervised work seems to be commoner in colleges than in secondary schools. But, until it is recognized and remedied, we can never secure either culture or a knowledge of chemistry * * * ."

In regard to the time for the introduction of the atomic theory he says (p. 161): "It may be possible to introduce the atomic theory at an early stage without causing confusion and to talk to beginners of atoms when combining weights are intended, without obscurity, but I do not know any text-book in which this has been done successfully, and I could name many in which it has been attempted with disastrous results."

The passages above quoted will meet with the hearty approval of a good many teachers of chemistry—among them the writer of this notice.

Finally, let me quote a part of what the author has to say on the subject of the importance of a knowledge of physical

chemistry for the teacher of chemistry: "On the whole, perhaps, after this discussion of some of the bearings of physical chemistry upon elementary chemistry, it may be a question whether, in the average course, time will be found for anything more than a touch of the subject here and there. The conclusion is inevitable, however, that the teacher himself must be thoroughly familiar with the results of physical chemistry and its applications to ordinary chemical phenomena, if the instruction he gives is to be thoroughly sound."

In the first part of the book, three misprints of proper names have been noted. On page 202, "F. W. Clark" should be "F. W. Clarke;" on page 221, "Ramay" should be "Ramsay;" on page 223, "Ritcher" should be "Richter."

Professor Hall's part of the book covers, to some extent, the same ground that Professor Smith's does, though the editor of the Series ("American Teachers Series"), Dr. James E. Russell, says: "The authors of the separate parts on chemistry and physics have conferred frequently during the progress of the work and have endeavored to avoid unnecessary duplication."

Professor Hall has had much to do with the working out of the Harvard *Descriptive List of Elementary Exercises in Physics*, and he naturally draws upon his experience in the use of this course, and those teachers who are following it should read what he has to say. The author says (page 315): "Physics is, at the best, hard for most minds, young or older; and if the teacher is blessed with the gift, or can by pains acquire the power, of presenting his subject in an attractive way, of making his teaching artistic in form as well as sound in substance, he will win not only the respect of his pupils but, what is perhaps to both sides more stimulating, their admiration." I. R.

TESTS AND REAGENTS, CHEMICAL AND MICROSCOPICAL. By ALFRED I. COHN, PH.G. New York: John Wiley & Sons. 1903. 8vo. pp. 383. Cloth, $3.00.

Chemists, and no doubt pharmacists and microscopists as well, are continually seeing in the literature references to tests and reagents that are known by their authors' names. It usually happens that the less common of them are not mentioned in the books at hand. The present work has been written with just this difficulty in view. The tests are arranged alphabetically, according to the names of the authors, and on the 338 pages devoted to them there are, on the average, 8 to the page. By far the greater number of these are of less importance to the chemist than to the other workers for

whom the book is intended. The following examples will give an idea of the character of the book: Lythgoe (aniline orange in milk); Magini (stain for nervous centers); Lux (fatty oils in mineral oils); Lawrence (glycerine jelly); Johnson (sugar in urine); Eboli (alkaloids); Edlefsen (naphthalene); Drechsler (alcohol); etc. In the index the substances tested for are given with the names of the authors following. Here and there errors in spelling occur. We note, for example, "Hoffmann." On the whole, the book seems to be a valuable one, and should be in demand.

C. E. W.

QUANTITATIVE CLASSIFICATION OF IGNEOUS ROCKS, Based on Chemical and Mineral Characters, with a Systematic Nomenclature by WHITMAN CROSS, JOSEPH P. IDDINGS, LOUIS V. PIRSSON, HENRY S. WASHINGTON. University of Chicago Press. pp. 286.

The publication of this work by four of the leading petrographers of America marks a distinct epoch in the study of igneous rocks and the handling of chemical analyses in petrographical investigations. The principles of classification involved call for the careful determination of the chemical constituents of each rock, and a computation of these into certain well-defined mineral molecules which are to be known as standard minerals. It is proposed to base the new classification on the predominant mineral constituents thus derived, which fall into two broad classes; the *salic* minerals, rich in silica and alumina, such as the feldspars, quartz, leucite, and nepheline, and the *femic* minerals, rich in iron and magnesium, such as diopside, hypersthene, olivine, etc. According to the proportions of these salic and femic minerals, igneous rocks are divided into five Classes. Each Class in turn is divided, according to the relative proportion of the minerals belonging to the predominant group, into five Orders, which are in turn divided into five Rangs, according to the ratio of $Na_2O + K_2O : CaO$ or $CaO + MgO + FeO : Na_2O$. The Rangs are in turn subdivided into five or three Subrangs according to the ratio of $K_2O : Na_2O$ and $MgO : FeO$. Each of the several divisions is indicated by a characteristic termination in the nomenclature.

The use of this classification will cause all rock masses of the same chemical composition to fall together in a purely artificial classification regardless of the minerals formed during the consolidation of the rock magma. The authors believe that a natural classification of rocks is not obtainable with our present knowledge, and suggest the new classification with the hope that it will avoid the present multiplication

of names and poorly defined rock types based upon mineralogical composition.

The adoption of this classification by the more advanced petrographers in America will necessitate greater accuracy in the analysis of the different chemical constituents, especially ferric and ferrous iron and the alkalies, as well as of the numerous constituents which are found in small quantities in igneous rocks, as shown by Hillebrand's excellent analyses.

E. B. M.

BENZOLTABELLEN. Darstellungsmethoden und Eigenschaften der einfacheren, technisch wichtigen Benzolderivate aus der Literature zusammengestellt von DR. CARL SCHWALBE, Privatdocenten an der Technischen Hochschule zu Darmstadt. Berlin: Gebrüder Borntraeger. 1903.

In this book of less than 270 quarto pages is contained a very large amount of information of value to every chemist who is interested in the derivatives of benzene and its homologues. The principal classes of compounds are taken up in order, beginning with the sulphonic acids, halogen derivatives, nitro derivatives, monamines, etc., and ending with the aldehydes, aldehydesulphonic acids, and the carbonic acids. Opening the book at random we come to 5-Sulphosalicylic acid. Under this heading are given six methods of formation of the acid, with references to the original literature in a parallel column. The properties are stated, again with literature references, and there are four articles cited in connection with the salts of the acid. Every one of the 250 or more compounds mentioned in the book is treated in a similar way. The book, apart from its large size, is not suited to the use of students in the laboratory on account of the brevity of the directions, but it will prove of great value to any one who wishes to learn the best methods of preparing benzene derivatives. It should find a place in every chemical library. C. E. W.

JAHRESBERICHT ÜBER DIE FORTSCHRITTE DER CHEMIE UND VERWANDTER THEILE ANDERER WISSENSCHAFTEN. Begründet von J. LIEBIG und H. KOPP. Unter Mitwirkung namhafter Fachgenossen herausgegeben von G. BODLÄNDER, W. KERP, und G. MINUNNI. Neuntes Heft. 1894. Braunschweig: Friedrich Vieweg und Sohn. 1902.

The "Jahresbericht" is so well known that its appearance calls for no comment except to note the fact that a new number has been issued. C. E. W.

LOIS GÉNÉRALES DE L'ACTION DES DIASTASES. Par VICTOR HENRI, Docteur en Philosophie (University de Göttingue), Docteur ès Sciences Préparateur de Physiologie a la Sorbonne. Paris: Librarie Scientifique A. Hermann. 1903. pp. 129.

The object of the author is to present the best work that

has been done on the kinetics of enzyme action, and to consider the results obtained in the light of what is known of the kinetics of more simple chemical reactions. In the introduction he very briefly summarizes the present knowledge of catalysis of which, as he says, enzyme action is but a special case.

Only three enzymes are considered in this work, namely, invertase, emulsin, and diastase. Chapter I. contains a review of what has been done on the kinetics of the above-mentioned enzymes, especially the work of O'Sullivan and Thompson, Tammann, Duclaux, A. Brown, H. Brown and Glendinning, and Herzog. The remaining 75 pages of the monograph deal with the work of the author, and his theoretical conclusions, which are of much interest and importance and may be summarized as follows:

Invertase.—(1) The inversion of saccharose by this enzyme is more rapid than would be indicated by the logarithmic equation which applies to the inversion by acids. (2) Invert sugar inhibits the action of invertase, and this inhibition is due almost entirely to the fructose. The inhibitory action of invert sugar is greatest when only a small amount of saccharose is present and decreases as the amount of saccharose is increased. (3) For solutions of saccharose more dilute than N/10, the velocity of the inversion increases with the concentration of the saccharose. Between N/10 and N/2 the velocity is independent of the concentration, while above N/2 increase in the concentration of the saccharose decreases the velocity of the inversion. (4) The velocity of the inversion is proportional to the quantity of enzyme acting. (5) The author assumes that the enzyme forms intermediate combinations with the substance upon which it acts, and also with the substances produced by its action. In support of this view he points out that Emil Fischer found invertase to act only on those substances which on hydrolysis yield fructose, and connects this with the fact that he has found that the inhibitory action of invert sugar is due almost entirely to fructose. He further points out that whereas the velocity of inversion is largely independent of the saccharose present at the beginning of the reaction, yet the addition of saccharose during the course of the reaction increases the velocity of the inversion. He explains the inhibitory effect of the products of enzyme action as Tammann did, *viz.*, by the formation of combinations between the enzyme and these products. He does not consider the question of reversibility as an explanation of inhibition by the products of hydrolysis. (6) He believes that

a state of equilibrium exists between the free enzyme and that combined with the substance upon which it acts and the products of the hydrolysis, and from this deduces the formula

$$\frac{dx}{dt} = \frac{k(a-x)}{1+m(a-x)+nx},$$

where k is a constant proportional to the quantity of enzyme acting, m and n are constants which depend upon the composition of the medium and the temperature, and vary with different enzymes. They give k the same value whatever be the concentration of the saccharose and invert sugar. This equation was found to hold for the action of invertase on saccharose and also for emulsin acting on salicin.

Emulsin.—He studied its action on salicin and found the hydrolysis to be slower than would be indicated by the logarithmic equation. Otherwise the results were similar to those given above for the action of invertase on saccharose.

Diastase.—(1) The velocity of the formation of maltose from starch by diastase follows a curve parallel to that of the acid hydrolysis. (2) The quantity of starch present influences in a different manner the action of pancreatic diastase and that obtained from malt. (3) It is impossible to treat this reaction mathematically since so little is known of the intermediate steps in the hydrolysis. (4) If we assume m and n to be equal in the above-mentioned equation, the formation of maltose seems to follow the same law as was found to hold for invertase and emulsin. A. S. L.

THE PRINCIPLES OF ANIMAL NUTRITION. With Special Reference to the Nutrition of Farm Animals. By HENRY PRENTISS ARMSBY, PH.D., Director of the Pennsylvania State College Agricultural Experiment Station; Expert in Animal Nutrition, United States Department of Agriculture, First edition; first thousand. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1903. pp. 614.

As the author states in his preface, this book is not a treatise upon stock-feeding, but "an attempt to present in systematic form to students of that subject a summary of our present knowledge of some of the fundamental principles of animal nutrition, particularly from the standpoint of energy relations, with special reference to their bearings upon the nutrition of farm animals."

It is assumed by the author that the reader is already familiar with the general nature of nutrition processes, and he, therefore, devotes all of his energy to that aspect of the subject of nutrition that has been designated by some writers as "the statistics of nutrition." Assuming the existence of a

fundamental distinction between matter and energy, the author divides the subject-matter into two parts. The first part deals with the income and expenditure of matter; the second part, with the income and expenditure of energy. The first two chapters of the first part deal quite generally with the essentials of feeding and of metabolism. Then, after devoting a chapter to a consideration of methods, the author discusses the subject of metabolism more minutely under the following heads, to each of which a chapter is devoted: Fasting Metabolism, The Relation of Metabolism to Food-supply, and The Influence of Muscular Exertion upon Metabolism. The plan outlined in the first part is adhered to in the second. After a general consideration in three chapters, of Force and Energy, of the Conservation of Energy in the Animal Body, and of Methods of Investigation, the main subject is developed in detail in the four remaining chapters, entitled: Food as a Source of Energy, Internal Work, Available Energy, and the Utilization of Energy.

The author handles these subjects with great skill. While the well-known facts are usually but briefly illustrated by a few classical experiments, the disputed points are discussed in detail, experiments and statistics are given at great length, together with full references to the literature. These discussions would be rather cumbersome were it not for the fact that each is concluded with a short and accurate summary, bringing all the data into a clear and concise paragraph or table.

The reviewer believes that workers in the field of animal nutrition will find the book of Dr. Armsby very valuable and suggestive, pointing out, as it does, the doubtful and the unknown in this branch of physiology. It is, however, to be regretted that the author adopts the classification of nitrogenous foodstuffs recommended by the Association of American Agricultural Colleges and Experiment Stations. Many of the terms used in this classification have totally different meanings in the classification now generally used by English, German, and American physiologists. J. E.